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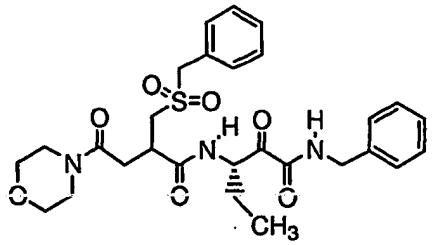
Thus, for example, in table 6 the compound denoted as A2-B4-C6-D8 is the product of the combination of group A2 in Table 1 and B4 in Table 2 and C6 in Table 3

and D8 in Table 4, namely *N*-[(S)-1-(1-benzylcarbamoyl-methanoyl)-propyl]-4-morpholin-4-yl-4-oxo-2-benzylsulfonylmethyl-butyramide:



Particular compounds of the invention are:

3-biphenyl-3-yl-*N*-cyanomethyl-2-benzylsulfonylmethyl-propionamide;

3-biphenyl-4-yl-*N*-cyanomethyl-2-benzylsulfonylmethyl-propionamide;

3-(3-bromo-phenyl)-*N*-cyanomethyl-2-benzylsulfonylmethyl-propionamide;

N-cyanomethyl-3-(3-cyano-benzylsulfonyl)-2-benzylsulfonyl-methyl-propionamide;

N-cyanomethyl-2-[2-1,1-difluoro-methoxy)-benzylsulfanylmethyl]-3-benzylsulfanyl-propionamide;

N-cyanomethyl-3-(2-trifluoromethyl-benzylsulfanyl)-2-(2-trifluoro-methyl-benzylsulfanylmethyl)-propionamide;

N-cyanomethyl-3-isobutylsulfanyl-2-isobutylsulfanylmethyl-propionamide;

N-cyanomethyl-4-phenylsulfanyl-2-(2-phenylsulfanyl-ethyl)-butyramide;

N-cyanomethyl-3-[2-(1,1-difluoro-methoxy)-benzylsulfanyl]-2-[2-(1,1-difluoro-methoxy)-benzylsulfanylmethyl]-propionamide;

3-benzylsulfanyl-2-benzylsulfanylmethyl-*N*-cyanomethyl-propionamide;

N-cyanomethyl-2-[2-1,1-difluoro-methoxy)-benzylsulfonylmethyl]-3-benzylsulfonyl-propionamide;

N-cyanomethyl-3-(2-trifluoromethyl-benzylsulfonyl)-2-(2-trifluoromethyl-benzylsulfonylmethyl)-propionamide;

4-benzenesulfonyl-2-(2-benzenesulfonyl-ethyl)-*N*-cyanomethyl-butyramide;

N-cyanomethyl-3-[2-(1,1-difluoro-methoxy)-benzylsulfonyl]-2-[2-(1,1-difluoro-methoxy)-benzylsulfonylmethyl]-propionamide;

N-cyanomethyl-3-benzylsulfonyl-2-benzylsulfonylmethyl-propionamide;

N-cyanomethyl-3-(2-methyl-propane-1-sulfonyl)-2-(2-methyl-propane-1-sulfonylmethyl)-propionamide;

N-cyanomethyl-3-(2-methyl-thiazol-4-ylmethylsulfonyl)-2-benzyl-sulfonylmethyl-propionamide;

3-biphenyl-3-yl-*N*-cyanomethyl-2-[2-(1,1-difluoro-methoxy)-benzyl-sulfonylmethyl]-propionamide;

(3'-{2-(cyanomethyl-carbamoyl)-3-[2-(1,1-difluoro-methoxy)-benzyl-sulfonyl]-propyl}-biphenyl-4-yl)-carbamic acid ethyl ester;

N-cyanomethyl-2-[2-(1,1-difluoro-methoxy)-benzylsulfonylmethyl]-3-(4'-methylsulfonylamino-biphenyl-3-yl)-propionamide;

3-(3-bromo-phenyl)-*N*-cyanomethyl-2-[2-(1,1-difluoro-methoxy)-phenyl-methylsulfonylmethyl]-propionamide;

N-cyanomethyl-2-((E)-3-phenyl-allyl)-3-benzylsulfonyl-propionamide;

N-cyanomethyl-3-benzylsulfonyl-2-(3-phenyl-propyl)-propionamide;

N-[(S)-1-(1-Benzooxazol-2-yl-methanoyl)-butyl]-3-benzylsulfonyl-2-benzylsulfonylmethyl-propionamide;

N-[(S)-1-(1-Benzooxazol-2-yl-methanoyl)-butyl]-3-(2-trifluoromethyl-benzylsulfonyl)-2-(2-trifluoromethyl-benzylsulfonylmethyl)-propionamide;

N-[(S)-1-(1-Benzooxazol-2-yl-methanoyl)-pentyl]-4-(2-methoxy-benzenesulfonyl)-2-[2-(2-methoxy-benzenesulfonyl)-ethyl]-butyramide;

4-Benzenesulfonyl-2-(2-benzenesulfonyl-ethyl)-*N*-[(S)-1-(1-benzooxazol-2-yl-methanoyl)-butyl]-butyramide;

(R)-*N*-[(S)-1-(1-benzooxazol-2-yl-methanoyl)-butyl]-2-cyclohexylmethyl-3-benzylsulfonyl-propionamide;

N-[(S)-1-(1-benzothiazol-2-yl-methanoyl)-propyl]-4-morpholin-4-yl-4-oxo-2-benzylsulfonylmethyl-butyramide;

N-[(S)-1-(1-benzooxazol-2-yl-methanoyl)-butyl]-3-cyclohexyl-2-cyclohexylmethyl-propionamide;

N-[(S)-1-(1-Benzooxazol-2-yl-methanoyl)-butyl]-3-isobutylsulfanyl-2-isobutylsulfanylmethyl-propionamide;

N-[(S)-1-(1-benzooxazol-2-yl-methanoyl)-butyl]-3-benzylsulfanyl-2-benzylsulfanylmethyl-propionamide;

N-[(S)-1-(1-benzooxazol-2-yl-methanoyl)-butyl]-4-phenylsulfanyl-2-(2-phenylsulfanyl-ethyl)-butyramide;

N-[(S)-1-(1-benzooxazol-2-yl-methanoyl)-propyl]-4-morpholin-4-yl-4-oxo-2-benzylsulfonylmethyl-butyramide;

N-[(S)-1-(1-Benzooxazol-2-yl-methanoyl)-pentyl]-4-morpholin-4-yl-4-oxo-2-benzylsulfonylmethyl-butyramide;

4-Morpholin-4-yl-4-oxo-2-benzylsulfonylmethyl-*N*-{(S)-1-[1-(3-phenyl-[1,2,4]oxadiazol-5-yl)-methanoyl]-propyl}-butyramide;

N-[(S)-1-(1-Benzooxazol-2-yl-methanoyl)-butyl]-2-[2-(1,1-difluoro-methoxy)-benzylsulfonylmethyl]-3-benzylsulfonyl-propionamide;

4-Morpholin-4-yl-4-oxo-*N*-[1-(2-oxo-2-phenyl-acetyl)-pentyl]-2-benzylsulfonylmethyl-butyramide;

N-(1,1-Dimethyl-2-oxazolo[4,5-b]pyridin-2-yl-2-oxo-ethyl)-4-morpholin-4-yl-4-oxo-2-benzylsulfonylmethyl-butyramide;

N-[1-(5-Ethyl-[1,3,4]oxadiazole-2-carbonyl)-butyl]-4-morpholin-4-yl-4-oxo-2-benzylsulfonylmethyl-butyramide;

N-[1-(5-Ethyl-[1,3,4]oxadiazole-2-carbonyl)-butyl]-4-oxo-2-benzylsulfonyl-methyl-4-piperidin-1-yl-butyramide;

N-[1-(5-Ethyl-[1,3,4]oxadiazole-2-carbonyl)-butyl]-4-oxo-2-benzylsulfonyl-methyl-4-pyrrolidin-1-yl-butyramide;

N-[1-(5-Methoxymethyl-[1,3,4]oxadiazole-2-carbonyl)-propyl]-4-morpholin-4-yl-4-oxo-2-benzylsulfonylmethyl-butyramide;

N-[1-(5-Methoxymethyl-[1,3,4]oxadiazole-2-carbonyl)-propyl]-4-oxo-2-benzylsulfonylmethyl-4-piperidin-1-yl-butyramide;

N-[1-(5-Methoxymethyl-[1,3,4]oxadiazole-2-carbonyl)-propyl]-4-oxo-2-benzylsulfonylmethyl-4-pyrrolidin-1-yl-butyramide;

4-Morpholin-4-yl-4-oxo-2-benzylsulfonylmethyl-*N*-[1-(5-phenyl-[1,3,4]oxadiazole-2-carbonyl)-propyl]-butyramide;

4-Oxo-2-benzylsulfonylmethyl-*N*-[1-(5-phenyl-[1,3,4]oxadiazole-2-carbonyl)-propyl]-4-piperidin-1-yl-butyramide;

4-Oxo-2-benzylsulfonylmethyl-*N*-[1-(5-phenyl-[1,3,4]oxadiazole-2-carbonyl)-propyl]-4-pyrrolidin-1-yl-butyramide;

4-Morpholin-4-yl-*N*-[1-(oxazolo[4,5-b]pyridine-2-carbonyl)-propyl]-4-oxo-2-benzylsulfonylmethyl-butyramide;

N-[1-(Oxazolo[4,5-b]pyridine-2-carbonyl)-propyl]-4-oxo-2-benzylsulfonyl-methyl-4-piperidin-1-yl-butyramide;

N-[1-(Oxazolo[4,5-b]pyridine-2-carbonyl)-propyl]-4-oxo-2-benzylsulfonyl-methyl-4-pyrrolidin-1-yl-butyramide;

4-Morpholin-4-yl-4-oxo-2-benzylsulfonylmethyl-*N*-[1-(5-pyridin-4-yl-[1,3,4]oxadiazole-2-carbonyl)-propyl]-butyramide;

4-Oxo-2-benzylsulfonylmethyl-4-piperidin-1-yl-*N*-[1-(5-pyridin-4-yl-[1,3,4]oxadiazole-2-carbonyl)-propyl]-butyramide;

4-Oxo-2-benzylsulfonylmethyl-*N*-[1-(5-pyridin-4-yl-[1,3,4]oxadiazole-2-carbonyl)-propyl]-4-pyrrolidin-1-yl-butyramide;

4-Morpholin-4-yl-4-oxo-2-benzylsulfonylmethyl-*N*-[1-(5-pyridin-3-yl-[1,3,4]oxadiazole-2-carbonyl)-propyl]-butyramide;

N-[1-(Benzooxazole-2-carbonyl)-propyl]-4-oxo-2-benzylsulfonylmethyl-4-piperidin-1-yl-butyramide;

N-[1-(Benzooxazole-2-carbonyl)-propyl]-4-oxo-2-benzylsulfonylmethyl-4-pyrrolidin-1-yl-butyramide;

N-[1-(Benzooxazole-2-carbonyl)-propyl]-2-cyclohexylmethyl-4-morpholin-4-yl-4-oxo-butyramide;

2-Cyclohexylmethyl-4-morpholin-4-yl-*N*-[1-(oxazolo[4,5-b]pyridine-2-carbonyl)-propyl]-4-oxo-butyramide;

2-Cyclohexylmethyl-N-[1-(5-ethyl-[1,3,4]oxadiazole-2-carbonyl)-butyl]-4-morpholin-4-yl-4-oxo-butyramide;

N-(2-Benzooxazol-2-yl-1-methoxymethyl-2-oxo-ethyl)-2-(2-difluoromethoxy-benzylsulfonylmethyl)-4-morpholin-4-yl-4-oxo-butyramide;

N-[1-(Benzooxazole-2-carbonyl)-propyl]-2-(2-cyclohexyl-ethyl)-4-morpholin-4-yl-4-oxo-butyramide;

2-(2-Cyclohexyl-ethyl)-4-morpholin-4-yl-*N*-[1-(oxazolo[4,5-b]pyridine-2-carbonyl)-propyl]-4-oxo-butyramide;

2-(2-Cyclohexyl-ethyl)-4-morpholin-4-yl-4-oxo-*N*-[1-(5-phenyl-[1,3,4]oxadiazole-2-carbonyl)-propyl]-butyramide;

2-(2-Difluoromethoxy-benzylsulfonylmethyl)-4-morpholin-4-yl-4-oxo-*N*-[1-(5-phenyl-[1,3,4]oxadiazole-2-carbonyl)-propyl]-butyramide;

2-(2-Difluoromethoxy-benzylsulfonylmethyl)-*N*-[1-(5-ethyl-[1,3,4]oxadiazole-2-carbonyl)-butyl]-4-morpholin-4-yl-4-oxo-butyramide;

N-[1-(Benzooxazole-2-carbonyl)-propyl]-2-(2-difluoromethoxy-benzyl-sulfonylmethyl)-4-morpholin-4-yl-4-oxo-butyramide;

2-(2-Morpholin-4-yl-2-oxo-ethyl)-5-phenyl-pentanoic acid,
1-(benzooxazole-2-carbonyl)-propyl]-amide;

(R)-2-Cyclohexylmethyl-4-morpholin-4-yl-4-oxo-*N*-[(S)-1-(5-phenyl-1,2,4-oxadiazole-3-carbonyl)-propyl]-butyramide;

2-(2-Morpholin-4-yl-2-oxo-ethyl)-5-phenyl-pentanoic acid,
(S)-1-(5-phenyl-[1,2,4]oxadiazole-3-carbonyl)-propyl]-amide;

4-Morpholin-4-yl-4-oxo-2-benzylsulfonylmethyl-*N*-[(S)-1-(5-phenyl-1,2,4-oxadiazole-3-carbonyl)-propyl]-butyramide;

(R)-2-Cyclohexylmethyl-4-morpholin-4-yl-4-oxo-*N*-[(S)-1-(3-phenyl-1,2,4-oxadiazole-5-carbonyl)-propyl]-butyramide;

4-Morpholin-4-yl-*N*-[1-(oxazole-2-carbonyl)-3-phenyl-propyl]-4-oxo-2-benzylsulfonylmethyl-butyramide;

N-(1,1-Dimethyl-2-oxazol-2-yl-2-oxo-ethyl)-4-morpholin-4-yl-4-oxo-2-benzylsulfonylmethyl-butyramide;

N-4-Isopropyl-*N*-1-[1-(oxazole-2-carbonyl)-3-phenyl-propyl]-2-benzylsulfonylmethyl-succinamide;

2-(2-Difluoromethoxy-benzylsulfonylmethyl)-4-morpholin-4-yl-*N*-[1-(oxazole-2-carbonyl)-3-phenyl-propyl]-4-oxo-butyramide;

2-(2-Methyl-propane-1-sulfonylmethyl)-4-morpholin-4-yl-*N*-[1-(oxazole-2-carbonyl)-3-

phenyl-propyl]-4-oxo-butyramide;

2-Cyclopropylmethylsulfonylmethyl-4-morpholin-4-yl-*N*-[1-(oxazole-2-carbonyl)-3-phenyl-propyl]-4-oxo-butyramide;

N-[1-(Benzooxazole-2-carbonyl)-butyl]-2-benzylsulfonyl-3-(tetrahydro-pyran-4-yloxymethyl)-propionamide;

N-[1-(Benzooxazole-2-carbonyl)-butyl]-3-ethanesulfonyl-2-(tetrahydro-pyran-4-yloxymethyl)-propionamide;

N-(1-Benzenesulfonyl-3-oxo-azepan-4-yl)-2-cyclopropylmethylsulfonyl-methyl-4-morpholin-4-yl-4-oxo-butyramide;

2-Cyclopropylmethylsulfonylmethyl-N-{(S)-1-[(R)-hydroxy-(3-phenyl-1,2,4-oxadiazol-5-yl)-methyl]-propyl}-4-morpholin-4-yl-4-oxo-butyramide;

N-{(S)-1-[(R)-hydroxy-(3-phenyl-1,2,4-oxadiazol-5-yl)-methyl]-propyl}-2-(2-methyl-propane-1-sulfonylmethyl)-4-morpholin-4-yl-4-oxo-butyramide;

2-(2-Morpholin-4-yl-2-oxo-ethyl)-5-phenyl-pentanoic acid {(S)-1-[(R)-hydroxy-(3-phenyl-1,2,4-oxadiazol-5-yl)-methyl]-propyl}-amide;

2-Cyclopropylmethylsulfonylmethyl-4-morpholin-4-yl-4-oxo-N-[(S)-1-(3-phenyl-1,2,4-oxadiazole-5-carbonyl)-propyl]-butyramide;

2-(2-methyl-propane-1-sulfonylmethyl)-4-morpholin-4-yl-4-oxo-N-[(S)-1-(3-phenyl-1,2,4-oxadiazole-5-carbonyl)-propyl]-butyramide;

2-(2-Morpholin-4-yl-2-oxo-ethyl)-5-phenyl-pentanoic acid, (S)-1-(3-phenyl-1,2,4-oxadiazole-5-carbonyl)-propyl}-amide;

N-[(1S)-1-(Benzooxazol-2-yl-hydroxy-methyl)-3-phenyl-propyl]-2-cyclopropylmethylsulfonylmethyl-4-morpholin-4-yl-4-oxo-butyramide;

(R)-2-((S)-1-Hydroxy-2-morpholin-4-yl-2-oxo-ethyl)-5-phenyl-pentanoic acid, 1-(benzoxazole-2-carbonyl)-propyl]-amide;

(R)-5-(2-Difluoromethoxy-phenyl)-2-((S)-1-hydroxy-2-morpholin-4-yl-2-oxo-ethyl)-pentanoic acid, 1-(benzoxazole-2-carbonyl)-propyl]-amide;

4-Morpholin-4-yl-N-[1-(oxazole-2-carbonyl)-cyclopropyl]-4-oxo-2-benzylsulfonyl methyl –butyramide;

N-[(S)-1-((E)-2-benzenesulfonyl-vinyl)-pentyl]-3-benzylsulfonyl-2-benzylsulfonylmethyl-propionamide

N-(3-benzenesulfonyl-1-phenethyl-allyl)-3-benzylsulfonyl-2-benzylsulfonylmethyl-propionamide;

N-(3-benzenesulfonylamino-2-oxo-propyl)-4-morpholin-4-yl-4-oxo-2-benzylsulfonylmethyl-butyramide;

(S)-2,2-difluoro-4-(4-morpholin-4-yl-4-oxo-2-benzylsulfonylmethyl-butanoylamino)-3-oxo-hexanoic acid dimethylamide;

N-[(S)-1-(1-Benzylcarbamoyl-methanoyl)-propyl]-3-benzylsulfonyl-2-benzylsulfonylmethyl-propionamide;

N-[(S)-1-(1-Benzylcarbamoyl-methanoyl)-propyl]-4-morpholin-4-yl-4-oxo-2-benzylsulfonylmethyl-butyramide;

3-Hydroxy-4-(4-morpholin-4-yl-4-oxo-2-benzylsulfonylmethyl-butyrylamino)-azepane-1-carboxylic acid tert-butyl ester;

4-(2-Cyclopropylmethylsulfonylmethyl-4-morpholin-4-yl-4-oxo-butyrylamino)-3-hydroxy-azepane-1-carboxylic acid tert-butyl ester;

3-Hydroxy-4-[2-(2-methyl-propane-1-sulfonylmethyl)-4-morpholin-4-yl-4-oxo-butyrylamino]-azepane-1-carboxylic acid tert-butyl ester;

4-(4-Morpholin-4-yl-4-oxo-2-benzylsulfonylmethyl-butyrylamino)-3-oxo-azepane-1-carboxylic acid tert-butyl ester;

4-(2-Cyclopropylmethylsulfonylmethyl-4-morpholin-4-yl-4-oxo-butyrylamino)-3-oxo-azepane-1-carboxylic acid tert-butyl ester;

4-[2-(2-Methyl-propane-1-sulfonylmethyl)-4-morpholin-4-yl-4-oxo-butyrylamino]-3-oxo-azepane-1-carboxylic acid tert-butyl ester;

N-(1-Benzenesulfonyl-3-oxo-azepan-4-yl)-4-morpholin-4-yl-4-oxo-2-benzylsulfonylmethyl-butyramide;

N-(1-Benzenesulfonyl-3-oxo-azepan-4-yl)-2-(2-methyl-propane-1-sulfonylmethyl)-4-morpholin-4-yl-4-oxo-butyramide;

3-(4-Morpholin-4-yl-4-oxo-2-benzylsulfonylmethyl-butyrylamino)-4-oxo-pyrrolidine-1-carboxylic acid tert-butyl ester;

4-(4-Morpholin-4-yl-4-oxo-2-benzylsulfonylmethyl-butyrylamino)-3-oxo-azepane-1-carboxylic acid benzyl ester;

acetic acid (2S,3S)-3-(4-morpholin-4-yl-4-oxo-2-benzylsulfonylmethyl-butanoylamino)-4-

oxo-azetidin-2-yl ester;and their corresponding N-oxides, and their prodrugs, and their protected derivatives, individual isomers and mixtures of isomers thereof; and the pharmaceutically acceptable salts and solvates (e.g. hydrates) of such compounds and their N-oxides and their prodrugs, and their protected derivatives, individual isomers and mixtures of isomers thereof.

Preferred compounds of the invention are:-

N-[(S)-1-(1-benzooxazol-2-yl-methanoyl)-butyl]-3-benzylsulfonyl-2-benzylsulfonylmethyl-propionamide (compound denoted as A64-B4-C11-D6), (Compound 1);

N-[(S)-1-(1-benzooxazol-2-yl-methanoyl)-butyl]-3-(2-trifluoromethyl-benzylsulfonyl)-2-(2-trifluoromethyl-benzylsulfonylmethyl)-propionamide, (compound denoted as A69-B32-C11-D6), (Compound 2);

N-[(S)-1-(1-benzooxazol-2-yl-methanoyl)-pentyl]-4-(2-methoxy-benzenesulfonyl)-2-[2-(2-methoxy-benzenesulfonyl)-ethyl]-butyramide, (compound denoted as A64-B85-C11-D6), (Compound 3);

4-benzenesulfonyl-2-(2-benzenesulfonyl-ethyl)-*N*-[(S)-1-(1-benzooxazol-2-yl-methanoyl)-butyl]-butyramide, (compound denoted as A4-B6-C11-D6), (Compound 4);

(R)-*N*-[(S)-1-(1-benzooxazol-2-yl-methanoyl)-butyl]-2-cyclohexylmethyl-3-benzylsulfonyl-propionamide, (Compound 5) ;

N-[(S)-1-(1-benzooxazol-2-yl-methanoyl)-butyl]-3-isobutylsulfanyl-2-isobutylsulfanylmethyl-propionamide, (compound denoted as A68-B79-C11-D6), (Compound 8);

N-[(S)-1-(1-benzooxazol-2-yl-methanoyl)-butyl]-3-benzylsulfanyl-2-benzylsulfanylmethyl-propionamide, (compound denoted as A64-B85-C11-D6), (Compound 9);

N-[(S)-1-(1-benzooxazol-2-yl-methanoyl)-butyl]-4-phenylsulfanyl-2-(2-phenylsulfanyl-ethyl)-butyramide, (compound denoted as A70-B80-C6-D6), (Compound 10);

N-cyanomethyl-2-[2-(1,1-difluoro-methoxy)-benzylsulfonylmethyl]-4-morpholin-4-yl-4-oxo-butyramide, (compound denoted as A2-B39-C1-D1), (Compound 25);

N-[(S)-1-(1-benzooxazol-2-yl-methanoyl)-propyl]-4-morpholin-4-yl-4-oxo-2-benzylsulfonylmethyl-butyramide, (compound denoted as A2-B4-C6-D6), (Compound 29);

N-[(S)-1-(1-benzooxazol-2-yl-methanoyl)-pentyl]-4-morpholin-4-yl-4-oxo-2-benzylsulfonylmethyl-butyramide, (compound denoted as A2-B4-C9-D6), (Compound 30);
N-[(S)-1-(1-benzylcarbamoyl-methanoyl)-propyl]-4-morpholin-4-yl-4-oxo-2-benzylsulfonylmethyl-butyramide, (compound denoted as A2-B4-C6-D8), (Compound 32);
N-[(S)-1-((E)-2-benzenesulfonyl-vinyl)-pentyl]-3-benzylsulfonyl-2-benzylsulfonylmethyl-propionamide, (compound denoted as A13-B4-C9-D7), (Compound 38);
N-(3-Benzenesulfonyl-1-phenethyl-allyl)-3-benzylsulfonyl-2-benzylsulfonylmethyl-propionamide, (compound denoted as A13-B4-C10-D7), (Compound 39) ;
N-cyanomethyl-3-(3-cyano-benzylsulfonyl)-2-benzylsulfonyl-methyl-propionamide, (compound denoted as A89-B4-C1-D1), (Compound 40);
4-morpholin-4-yl-4-oxo-2-benzylsulfonylmethyl-*N*-{(S)-1-[1-(3-phenyl-[1,2,4]oxadiazol-5-yl)-methanoyl]-propyl}-butyramide, (compound denoted as A2-B4-C6-D10), (Compound 41);
N-cyanomethyl-2-[2-1,1-difluoro-methoxy)-benzylsulfonylmethyl]-3-benzylsulfonyl-propionamide, (compound denoted as A13-B39-C1-D1), (Compound 48);
N-cyanomethyl-3-[2-(1,1-difluoro-methoxy)-benzylsulfonyl]-2-[2-(1,1-difluoro-methoxy)-benzylsulfonylmethyl]-propionamide, (compound denoted as A5-B39-C1-D1), (Compound 51);
N-[(S)-1-(1-benzylcarbamoyl-methanoyl)-propyl]-3-benzylsulfonyl-2-benzylsulfonylmethyl-propionamide, (compound denoted as A13-B4-C6-D8), (Compound 53);
N-[(S)-1-(1-benzooxazol-2-yl-methanoyl)-butyl]-2-[2-(1,1-difluoro-methoxy)-benzylsulfonylmethyl]-3-benzylsulfonyl-propionamide, (compound denoted as A13-B39-C11-D6), (Compound 54);
acetic acid (2S,3S)-3-(4-morpholin-4-yl-4-oxo-2-benzylsulfonylmethyl-butanoylamino)-4-oxo-azetidin-2-yl ester, (compound denoted as A2-B4-E4), (Compound 58);
N-cyanomethyl-3-(2-methyl-thiazol-4-ylmethylsulfonyl)-2-benzyl-sulfonylmethyl-propionamide, (compound denoted as A114-B4-C1-D1), (Compound 59);

and the N-oxide derivatives, prodrug derivatives, protected derivatives, individual stereoisomers and mixtures of isomers thereof; and the pharmaceutically acceptable salts and solvates (e.g. hydrates) of such compounds and the N-oxide derivatives, prodrug

derivatives, protected derivatives, individual isomers and mixtures of isomers thereof.

Especially preferred compounds of the invention are:-

N-[(S)-1-(1-benzooxazol-2-yl-methanoyl)-butyl]-3-benzylsulfonyl-2-benzylsulfonylmethyl-propionamide (compound denoted as A64-B4-C11-D6), (Compound 1);

4-benzenesulfonyl-2-(2-benzenesulfonyl-ethyl)-*N*-[(S)-1-(1-benzooxazol-2-yl-methanoyl)-butyl]-butyramide, (compound denoted as A4-B6-C11-D6), (Compound 4);

N-[(S)-1-(1-benzooxazol-2-yl-methanoyl)-propyl]-4-morpholin-4-yl-4-oxo-2-benzylsulfonylmethyl-butyramide (compound denoted as A2-B4-C6-D6), (Compound 29);

N-[(S)-1-(1-benzooxazol-2-yl-methanoyl)-pentyl]-4-morpholin-4-yl-4-oxo-2-benzylsulfonylmethyl-butyramide, (compound denoted as A2-B4-C9-D6), (Compound 30);

N-[(S)-1-(1-benzylcarbamoyl-methanoyl)-propyl]-4-morpholin-4-yl-4-oxo-2-benzylsulfonylmethyl-butyramide, (compound denoted as A2-B4-C6-D8), (Compound 32);

N-[(S)-1-((E)-2-benzenesulfonyl-vinyl)-pentyl]-3-benzylsulfonyl-2-benzylsulfonylmethyl-propionamide, (compound denoted as A13-B4-C9-D7), (Compound 38);

N-(3-Benzenesulfonyl-1-phenethyl-allyl)-3-benzylsulfonyl-2-benzylsulfonylmethyl-propionamide, (compound denoted as A13-B4-C10-D7), (Compound 39) ;

4-morpholin-4-yl-4-oxo-2-benzylsulfonylmethyl-*N*-{(S)-1-[1-(3-phenyl-[1,2,4]oxadiazol-5-yl)-methanoyl]-propyl}-butyramide, (compound denoted as A2-B4-C6-D10), (Compound 41);

N-[(S)-1-(1-benzylcarbamoyl-methanoyl)-propyl]-3-benzylsulfonyl-2-benzylsulfonylmethyl-propionamide, (compound denoted as A13-B4-C6-D8), (Compound 53);

N-[(S)-1-(1-benzooxazol-2-yl-methanoyl)-butyl]-2-[2-(1,1-difluoro-methoxy)-benzylsulfonylmethyl]-3-benzylsulfonyl-propionamide, (compound denoted as A13-B39-C11-D6), (Compound 54);

and the N-oxide derivatives, prodrug derivatives, protected derivatives, individual stereoisomers and mixtures of isomers thereof; and the pharmaceutically acceptable salts and solvates (e.g. hydrates) of such compounds and the N-oxide derivatives, prodrug derivatives, protected derivatives, individual isomers and mixtures of isomers thereof.

Pharmacology and Utility:

The compounds of the invention are selective inhibitors of cathepsin S and, as such, are useful for treating diseases in which cathepsin S activity contributes to the pathology and/or symptomatology of the disease. For example, the compounds of the invention are useful in treating autoimmune disorders, including, but not limited to, juvenile onset diabetes, multiple sclerosis, pemphigus vulgaris, Graves' disease, myasthenia gravis, systemic lupus erythemotasus, rheumatoid arthritis and Hashimoto's thyroiditis, allergic disorders, including, but not limited to, asthma, and allogeneic immune responses, including, but not limited to, organ transplants or tissue grafts.

Cathepsin S also is implicated in disorders involving excessive elastolysis, such as chronic obstructive pulmonary disease (e.g., emphysema), bronchiolitis, excessive airway elastolysis in asthma and bronchitis, pneumonities and cardiovascular disease such as plaque rupture and atheroma. Cathepsin S is implicated in fibril formation and, therefore, inhibitors of cathepsins S are of use in treatment of systemic amyloidosis.

The cysteine protease inhibitory activities of the compounds of the invention can be determined by methods known to those of ordinary skill in the art. Suitable *in vitro* assays for measuring protease activity and the inhibition thereof by test compounds are known. Typically, the assay measures protease-induced hydrolysis of a peptide-based substrate. Details of assays for measuring protease inhibitory activity are set forth in Examples 69, 70, 71 and 72, *infra*.

Administration and Pharmaceutical Compositions:

In general, compounds of Formula I will be administered in therapeutically effective amounts via any of the usual and acceptable modes known in the art, either singly or in combination with one or more therapeutic agents. A therapeutically effective amount may vary widely depending on the severity of the disease, the age and relative health of the subject, the potency of the compound used and other factors. For example, therapeutically effective amounts of a compound of Formula I may range from about 1 micrograms per kilogram body weight (μg/kg) per day to about 1 milligram per kilogram body weight (mg/kg) per day, typically from about 10 μg/kg/day to about 0.1 mg/kg/day. Therefore, a therapeutically effective amount for a 80 kg human patient may range from about 100

μg/day to about 100 mg/day, typically from about 1 μg/day to about 10 mg/day. In general, one of ordinary skill in the art, acting in reliance upon personal knowledge and the disclosure of this Application, will be able to ascertain a therapeutically effective amount of a compound of Formula I for treating a given disease.

The compounds of Formula I can be administered as pharmaceutical compositions by one of the following routes: oral, systemic (e.g., transdermal, intranasal or by suppository) or parenteral (e.g., intramuscular, intravenous or subcutaneous). Compositions can take the form of tablets, pills, capsules, semisolids, powders, sustained release formulations, solutions, suspensions, elixirs, aerosols, or any other appropriate composition and are comprised of, in general, a compound of Formula I in combination with at least one pharmaceutically acceptable excipient. Acceptable excipients are non-toxic, aid administration, and do not adversely affect the therapeutic benefit of the active ingredient. Such excipient may be any solid, liquid, semisolid or, in the case of an aerosol composition, gaseous excipient that is generally available to one of skill in the art.

Solid pharmaceutical excipients include starch, cellulose, talc, glucose, lactose, sucrose, gelatin, malt, rice, flour, chalk, silica gel, magnesium stearate, sodium stearate, glycerol monostearate, sodium chloride, dried skim milk, and the like. Liquid and semisolid excipients may be selected from water, ethanol, glycerol, propylene glycol and various oils, including those of petroleum, animal, vegetable or synthetic origin (e.g., peanut oil, soybean oil, mineral oil, sesame oil, and the like). Preferred liquid carriers, particularly for injectable solutions, include water, saline, aqueous dextrose and glycols.

The amount of a compound of Formula I in the composition may vary widely depending upon the type of formulation, size of a unit dosage, kind of excipients and other factors known to those of skill in the art of pharmaceutical sciences. In general, a composition of a compound of Formula I for treating a given disease will comprise from 0.01%w to 10%w, preferably 0.3%w to 1%w, of active ingredient with the remainder being the excipient or excipients. Preferably the pharmaceutical composition is administered in a single unit dosage form for continuous treatment or in a single unit dosage form ad libitum when relief of symptoms is specifically required. Representative pharmaceutical formulations containing a compound of Formula I are described in Example 73.

Chemistry:

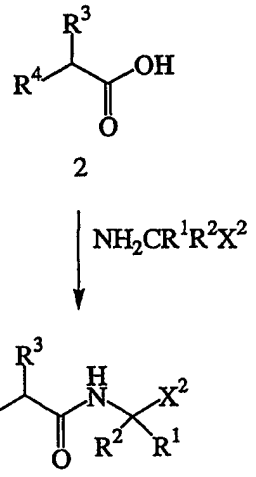
Processes for Making Compounds of Formula I:

Compounds of the invention may be prepared by the application or adaptation of known methods, by which is meant methods used heretofore or described in the literature, for example those described by R.C. Larock in Comprehensive Organic Transformations, VCH publishers, 1989.

In the reactions described hereinafter it may be necessary to protect reactive functional groups, for example hydroxy, amino, imino, thio or carboxy groups, where these are desired in the final product, to avoid their unwanted participation in the reactions. Conventional protecting groups may be used in accordance with standard practice, for examples see T.W. Greene and P. G. M. Wuts in "Protective Groups in Organic Chemistry" John Wiley and Sons, 1991.

Compounds of Formula I, where X^1 is $-NHC(R^1)(R^2)X^2$, can be prepared by proceeding as in the following Reaction Scheme 1:

Reaction Scheme 1



I

in which each X^2, R^1, R^2, R^3 and R^4 are as defined for Formula I in the Summary of the

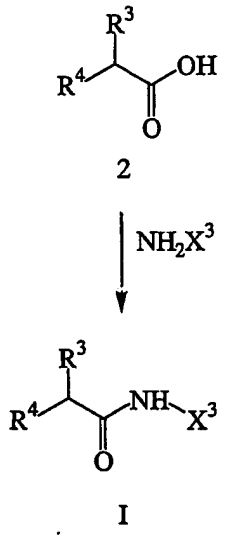
Invention.

Compounds of Formula I can be prepared by condensing an acid of Formula 2 with an amino compound of formula $NH_2CR^1R^2X^2$. The condensation reaction can be effected with an appropriate coupling agent (e.g., benzotriazol-1-yloxytrispyrrolidinophosphonium hexafluorophosphate (PyBOP®), 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDCI), *O*-benzotriazol-1-yl-*N*,*N*,*N*',*N*'-tetramethyluronium hexafluorophosphate (HBTU), 1,3-dicyclohexylcarbodiimide (DCC), or the like) and optionally an appropriate catalyst (e.g., 1-hydroxybenzotriazole (HOBt), 1-hydroxy-7-azabenzotriazole (HOAt), *O*-(7-azabenzotrizol-1-yl)-1,1,3,3, tetra-methyluroniumhexafluorophosphate (HATU), or the like) and non-nucleophilic base (e.g., triethylamine, *N*-methylmorpholine, and the like, or any suitable combination thereof) at ambient temperature and requires 5 to 10 hours to complete.

An oxidation step, if required, can be carried out with an oxidizing agent (e.g., Oxone®, metachloroperbenzoic acid or the like) in a suitable solvent (e.g., methanol, water, or the like, or any suitable combination thereof) at ambient temperature and requires 16 to 24 hours to complete. Detailed descriptions for the synthesis of a compound of Formula I by the processes in Reaction Scheme 1 are set forth in the Examples 1 to 6, *infra*.

Compounds of Formula I, where X^1 is $-NHX^3$, can be prepared by proceeding as in the following Reaction Scheme 2:

Reaction Scheme 2

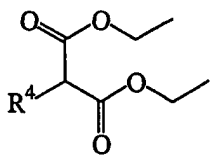


in which each X^3, R^3 and R^4 are as defined for Formula I in the Summary of the Invention.

Compounds of Formula I can be prepared by condensing an acid of Formula 2 with an amino compound of formula NH_2X^3. The condensation reaction can be effected with an appropriate coupling agent (e.g., benzotriazol-1-yloxytrispyrrolidinophosphonium hexafluorophosphate (PyBOP®), 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDCI), *O*-benzotriazol-1-yl-*N*,*N*,*N*',*N*'-tetramethyluronium hexafluorophosphate (HBTU), 1,3-dicyclohexylcarbodiimide (DCC), or the like) and optionally an appropriate catalyst (e.g., 1-hydroxybenzotriazole (HOBt), 1-hydroxy-7-azabenzotriazole (HOAt), *O*-(7-azabenzotrizol-1-yl)-1,1,3,3, tetra-methyluroniumhexafluorophosphate (HATU), or the like) and non-nucleophilic base (e.g., triethylamine, *N*-methylmorpholine, and the like, or any suitable combination thereof) at ambient temperature and requires 5 to 10 hours to complete.

An oxidation step, if required, can be carried out with an oxidizing agent (e.g., Oxone®, metachloroperbenzoic acid or the like) in a suitable solvent (e.g., methanol, water, or the like, or any suitable combination thereof) at ambient temperature and requires 16 to 24 hours to complete.

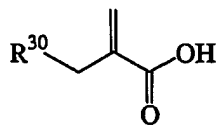
Compounds of Formula 2 can be prepared by reacting a compound of Formula 3 with a compound of Formula R^3L:



3

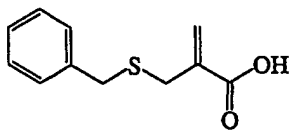
in which L is a leaving group and R^3 and R^4 are as defined in the Summary of the Invention. The reaction involves coupling (or alkylation) followed by alkaline hydrolysis at a temperature during which the dicarboxylic acid formed undergoes mono-decarboxylation. The coupling reaction can be carried out in the presence of a suitable base (e.g. triethylamine) in a suitable solvent (e.g. ethanol). The decarbalkoxylation can be effected under strongly basic conditions (e.g. in the presence of 1N aqueous sodium hydroxide) in a suitable solvent (e.g. ethanol). Detailed descriptions for the synthesis of compounds of Formula 2 by the process described above are set forth in the References, *infra*.

Compounds of Formula 2, in which R^3 and R^4 are benzylsulfonylmethyl, can be prepared by reacting a compound of Formula 4:



4

in which R^{30} is a halo group, with benzyl mercaptan under strongly basic conditions to produce a compound of Formula 5:

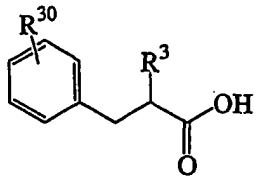


5

followed by reaction with benzyl mercaptan in the presence of a suitable coupling reagent

(e.g. DMAP) and in a suitable solvent (e.g. DMF). A detailed description of the synthesis of a compound of Formula 2 by a similar process as that described above is set forth in the References, *infra*.

Compounds of Formula 2, in which R^4 is biaryl, can be prepared by coupling a compound of Formula 6:



6

in which R^{30} is a halo group and R^3 is as defined in the Summary of the Invention, with a compound of ArL, in which Ar is an aryl group and L is a leaving group, to produce a compound of Formula 2 in which R^4 is biaryl. The coupling reaction takes place in the presence of a suitable catalyst (e.g. tetrakis-triphenylphosphine palladium). A detailed description of the synthesis of a compound of Formula 2 by the process described above is set forth in the References, *infra*.

Additional Processes for Preparing Compounds of Formula I:

A compound of Formula I can be prepared as a pharmaceutically acceptable acid addition salt by reacting the free base form of the compound with a pharmaceutically acceptable inorganic or organic acid. Alternatively, a pharmaceutically acceptable base addition salt of a compound of Formula I can be prepared by reacting the free acid form of the compound with a pharmaceutically acceptable inorganic or organic base. Inorganic and organic acids and bases suitable for the preparation of the pharmaceutically acceptable salts of compounds of Formula I are set forth in the definitions section of this Application. Alternatively, the salt forms of the compounds of Formula I can be prepared using salts of the starting materials or intermediates.

The free acid or free base forms of the compounds of Formula I can be prepared from the corresponding base addition salt or acid addition salt form. For example, a compound of Formula I in an acid addition salt form can be converted to the corresponding

free base by treating with a suitable base (e.g., ammonium hydroxide solution, sodium hydroxide, and the like). A compound of Formula I in a base addition salt form can be converted to the corresponding free acid by treating with a suitable acid (e.g., hydrochloric acid, etc).

The *N*-oxides of compounds of Formula I can be prepared by methods known to those of ordinary skill in the art. For example, *N*-oxides can be prepared by treating an unoxidized form of the compound of Formula I with an oxidizing agent (e.g., trifluoroperacetic acid, permaleic acid, perbenzoic acid, peracetic acid, *meta*-chloroperoxybenzoic acid, or the like) in a suitable inert organic solvent (e.g., a halogenated hydrocarbon such as dichloromethyl) at approximately 0°C. Alternatively, the *N*-oxides of the compounds of Formula I can be prepared from the *N*-oxide of an appropriate starting material.

Compounds of Formula I in unoxidized form can be prepared from *N*-oxides of compounds of Formula I by treating with a reducing agent (e.g., sulfur, sulfur dioxide, triphenyl phosphine, lithium borohydride, sodium borohydride, phosphorus trichloride, tribromide, or the like) in an suitable inert organic solvent (e.g., acetonitrile, ethanol, aqueous dioxane, or the like) at 0 to 80°C.

Prodrug derivatives of the compounds of Formula I can be prepared by methods known to those of ordinary skill in the art (e.g., for further details see Saulnier *et al.*(1994), *Bioorganic and Medicinal Chemistry Letters*, Vol. 4, p. 1985). For example, appropriate prodrugs can be prepared by reacting a non-derivatized compound of Formula I with a suitable carbamylating agent (e.g., 1,1-acyloxyalkylcarbonochloridate, *para*-nitrophenyl carbonate, or the like).

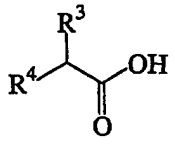
Protected derivatives of the compounds of Formula I can be made by means known to those of ordinary skill in the art. A detailed description of the techniques applicable to the creation of protecting groups and their removal can be found in T.W. Greene, *Protecting Groups in Organic Synthesis*, 3rd edition, John Wiley & Sons, Inc. 1999.

Compounds of the present invention may be conveniently prepared, or formed during the process of the invention, as solvates (e.g. hydrates). Hydrates of compounds of the present invention may be conveniently prepared by recrystallisation from an aqueous/organic solvent mixture, using organic solvents such as dioxin, tetrahydrofuran or methanol.

Compounds of Formula I can be prepared as their individual stereoisomers by reacting a racemic mixture of the compound with an optically active resolving agent to form a pair of diastereoisomeric compounds, separating the diastereomers and recovering the optically pure enantiomer. While resolution of enantiomers can be carried out using covalent diasteromeric derivatives of compounds of Formula I, dissociable complexes are preferred (e.g., crystalline diastereoisomeric salts). Diastereomers have distinct physical properties (e.g., melting points, boiling points, solubilities, reactivity, etc.) and can be readily separated by taking advantage of these dissimilarities. The diastereomers can be separated by chromatography or, preferably, by separation/resolution techniques based upon differences in solubility. The optically pure enantiomer is then recovered, along with the resolving agent, by any practical means that would not result in racemization. A more detailed description of the techniques applicable to the resolution of stereoisomers of compounds from their racemic mixture can be found in Jean Jacques Andre Collet, Samuel H. Wilen, Enantiomers, Racemates and Resolutions, John Wiley & Sons, Inc. (1981).

In summary, the compounds of Formula I are made by a process which comprises:

(A) reacting a compound of Formula 2:



2

with a compound of the formula $NH_2CR^1R^2X^2$, in which X^2, R^1, R^2, R^3 and R^4 are as defined in the Summary of the Invention for Formula I; or

(B) reacting a compound of Formula 2 with a compound of the formula NH_2X^3, in which X^3, R^3 and R^4 are as defined in the Summary of the Invention for Formula I; or

(C) optionally converting a compound of Formula I into a pharmaceutically acceptable salt;

(D) optionally converting a salt form of a compound of Formula I to non-salt form;

(E) optionally converting an unoxidized form of a compound of Formula I into a pharmaceutically acceptable *N*-oxide;

(F) optionally converting an *N*-oxide form of a compound of Formula I its unoxidized form;

(G) optionally resolving an individual isomer of a compound of Formula I from a mixture of isomers;

(H) optionally converting a non-derivatized compound of Formula I into a pharmaceutically prodrug derivative; and

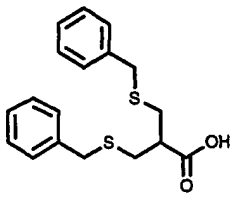
(I) optionally converting a prodrug derivative of a compound of Formula I to its non-derivatized form.

Examples:

The present invention is further exemplified, but not limited by, the following examples that illustrate the preparation of compounds of Formula I (Examples) and intermediates (References) according to the invention.

REFERENCE 1

3-Benzylsulfanyl-2-benzylsulfanylmethyl-propionic acid



A solution of diethyl bis(hydroxymethyl)malonate (46.95g, 0.21 moles) (prepared by the method of P. Block, Jr., Organic Synthesis, Collective Volume V, 381 (1973)) in methylene chloride (500mL) was treated with triethylamine (63mL) and cooled to –30°C. A mixture of methylsulfonyl chloride (35 mL) in methylene chloride (40 mL) was added to the reaction mixture dropwise over 20 minutes and the reaction mixture was allowed to stir

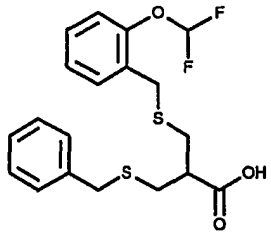
at room temperature for 18 hours. The reaction mixture was then poured into ice water and the product was extracted with methylene chloride. The organic extracts were washed with saturated aqueous sodium chloride and then dried over magnesium sulfate. The solvent was removed by rotary evaporation at reduced pressure and the residue was recrystallized from t-butylmethyl ether and hexane to give 2,2-bis-methylsulfonyloxymethyl-malonic acid diethyl ester (55.04 g).

Sodium (0.268 g, 11.6 mmol) was dissolved in ethanol (25 mL) and the resulting solution was treated with benzyl mercaptan (1.87 mL, 15.9 mmol). The reaction mixture was cooled on ice and the 2,2-bis-methylsulfonyloxymethyl-malonic acid diethyl ester (2.00g, 5.31 mmol) was added. The reaction mixture was stirred at room temperature for 16 hours and then heated at 55°C for 1.5 hours. The resulting solution was cooled to room temperature and poured into ice water. The product was extracted with ethyl acetate. The extracts were washed with saturated aqueous sodium chloride and then dried over magnesium sulfate. The solvent was removed by rotary evaporation at reduced pressure and the residue was chromatographed on silica gel eluting with ethyl acetate/hexane to give 3-benzylsulfanyl-2-benzylsulfanylmethyl-propionic acid ethyl ester (1.589 g, 83% yield).

3-Benzylsulfanyl-2-benzylsulfanylmethyl-propionic acid ethyl ester (1.589 g, 4.41 mmol) in a mixture of potassium hydroxide (1N, 7 mL), water (3 mL), dioxane (30 mL) and ethanol (10 mL) was stirred at room temperature for 18 hours. The solvents were removed form the reaction mixture by rotary evaporation at reduced pressure and the residue was dissolved in water and washed with ether. The aqueous layer was cooled on ice, acidified to pH 2 and the product extracted with ethyl acetate. The extracts were washed with saturated aqueous sodium chloride and then dried over magnesium sulfate. The solvent was removed by rotary evaporation at reduced pressure to give 3-benzylsulfanyl-2-benzylsulfanylmethyl-propionic acid (1.293g, 88%).

REFERENCE 2

2-Benzylsulfanylmethyl-3-[2-(1,1-difluoro-methoxy)-benzylsulfanyl]-propionic acid

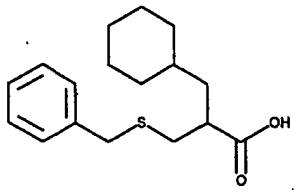


2-Bromomethylacrylic acid (3.00 g, 18.1 mmol) was dissolved in methanol (100mL), cooled on an ice bath and treated with benzyl mercaptan. Aqueous sodium hydroxide (1N, 39.8 mL) was added dropwise and the reaction mixture was allowed to adjust to room temperature with stirring for 23 hours. Methanol was removed by rotary evaporation at reduced pressure and water (100 mL) was added to the residue, which was then washed with ether. The aqueous layer was cooled on ice and acidified to pH 2.5. The precipitated solid was isolated by filtration and dried to give 2-benzylsulfanylmethyl-acrylic acid (3.346 g, 89 %).

A solution of 2-difluoromethoxybenzyl mercaptan (0.534 g, 2.81 mmol), 2-benzylsulfanylmethyl-acrylic acid (0.585 g, 2.81 mmol) and 4-dimethylaminopyridine (36 mg, 0.3 mmol) in DMF (1.5 ml) was stirred at room temperature for 20 hours. An additional amount of 2-difluoromethoxybenzyl mercaptan (0.201 g) was added to the reaction mixture and stirring was continued for another 24 hours. The reaction mixture was poured into dilute, cold, aqueous HCl and the product extracted with ethyl acetate. The extracts were washed with saturated aqueous sodium chloride and then dried over magnesium sulfate. The solvent was removed by rotary evaporation at reduced pressure and the residue was chromatographed on silica gel eluting with ethyl acetate/hexane to give 2-Benzylsulfanylmethyl-3-[2-(1,1-difluoro-methoxy)-benzylsulfanyl]-propionic acid (0.706 g).

REFERENCE 3

2-Benzylsulfanylmethyl-3-cyclohexyl-propionic acid



A solution of diethyl-2-cyclohexylmethyl malonate (2.56 g), 37% aqueous formaldehyde (0.80 mL), potassium bicarbonate (0.08g) and ethanol (2.5 mL) was stirred at room temperature for 20 hours. Saturated aqueous ammonium sulfate (10 mL) was added to the reaction and the product extracted with ethyl acetate. The extracts were washed with saturated aqueous sodium chloride and then dried over magnesium sulfate. The solvent was removed by rotary evaporation at reduced pressure and the residue was chromatographed on silica gel eluting with ethyl acetate/hexane to give 2-cyclohexylmethyl-2-hydroxymethyl-malonic acid diethyl ester (1.31g).

A solution of 2-cyclohexylmethyl-2-hydroxymethyl-malonic acid diethyl ester (1.31 g, 4.13 mmol) in methylene chloride (20 mL) and triethyl amine (1.16 mL, 8.00 mmol) was cooled to -40°C. A solution of methylsulfonyl chloride (0.402 mL, 5.2 mmol) in methylene chloride (4 mL) was added to the reaction mixture over 5 minutes. The reaction mixture was warmed to -10°C over 1 hour and then poured into cold dilute aqueous HCl. The product was extracted with ethyl acetate, the extracts were washed with saturated aqueous sodium chloride and then dried over magnesium sulfate. The solvent was removed by rotary evaporation at reduced pressure to give 2-cyclohexylmethyl-2-methylsulfonyloxymethyl-malonic acid diethyl ester (1.505 g).

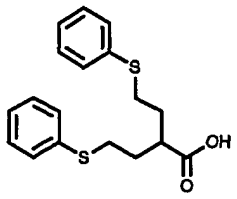
Sodium (0.097 g, 4.2 mmol) was dissolved in ethanol (10 mL) and the resulting solution was cooled to 0°C and treated with a mixture comprising benzyl mercaptan (0.493 mL, 4.2 mmol) and 2-cyclohexylmethyl-2-methylsulfonyloxymethyl-malonic acid diethyl ester (1.466 g, 4.02 mmol). The reaction was stirred at room temperature for 17 hours, 53°C for 20 hours and 73°C for 24 hours. The ethanol was removed by rotary evaporation, the reaction mixture was poured into water and the product was extracted with ethyl acetate. The extracts were washed with saturated aqueous sodium chloride and then dried over magnesium sulfate. The solvent was removed by rotary evaporation at reduced

pressure and the residue was chromatographed on silica gel eluting with ethyl acetate/hexane to give 2-benzylsulfanylmethyl-3-cyclohexyl-propionic acid ethyl ester (0.237 g).

A mixture of 2-benzylsulfanylmethyl-3-cyclohexyl-propionic acid ethyl ester (0.230g), dioxane (10 mL), sodium hydroxide (1N, 3 mL), water (2 mL) and ethanol (4 mL) was stirred for 20 hours at room temperature. The solvents were evaporated and the residue dissolved in water (50 mL). The aqueous solution was washed twice with ether and then acidified to pH2. The product was extracted from the aqueous solution with ethyl acetate and the extracts were washed with saturated aqueous sodium chloride and then dried over magnesium sulfate. The solvent was removed by rotary evaporation at reduced pressure to give acid 2-benzylsulfanylmethyl-3-cyclohexyl-propionic acid (0.210 g).

REFERENCE 4

4-Benzenesulfonyl-2-(2-benzenesulfonyl-ethyl)-butyric acid



A mixture of 2-iodoethylphenyl sulfide (19.81g, 75mmol), diethyl malonate (4.80g, 30mmol), potassium carbonate (10.35g, 75mmol) and DMF (40mL) was heated at 52°C for 18 hours. More potassium carbonate (10g) was added and the reaction was continued at 52°C for another 8 hours. The reaction mixture was cooled, diluted with ice water and the product extracted with ethyl acetate. The extracts were washed with saturated aqueous sodium chloride and then dried over magnesium sulfate. The solvent was removed by rotary evaporation at reduced pressure and the residue was chromatographed on silica gel eluting with ethyl acetate/hexane to give 2,2-bis-(2-phenylsulfanyl-ethyl)-malonic acid diethyl ester (5.648g).

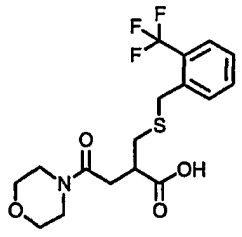
A solution of 2,2-bis-(2-phenylsulfanyl-ethyl)-malonic acid diethyl ester (5.614g) in ethanol (100mL) was treated with lithium hydroxide (2.84g) in water (10mL). The reaction mixture was heated at 49°C for 17 hours followed by 85°C for 2 hours. The solvents were evaporated at reduced pressure to give a residue that was treated with water (100mL) and washed with ether. The aqueous layer was cooled on ice, acidified and the product extracted with ethyl acetate. The extracts were dried over magnesium sulfate. The solvent was removed by rotary evaporation at reduced pressure to give acid 2,2-bis-(2-phenylsulfanyl-ethyl)-malonic acid (5.628 g).

2,2-Bis-(2-phenylsulfanyl-ethyl)-malonic acid (5.628 g) was heated at 150°C for 30 minutes. The reaction mixture was cooled to room temperature, dissolved in ethyl acetate and washed with aqueous sodium bicarbonate. The ethyl acetate solution was washed with saturated aqueous sodium chloride and then dried over magnesium sulfate. The solvent was removed by rotary evaporation at reduced pressure and the residue was chromatographed on silica gel eluting with ethyl acetate/hexane to give 4-phenylsulfanyl-2-(2-phenylsulfanyl-ethyl)-butyric acid (1.831 g).

A solution of 4-phenylsulfanyl-2-(2-phenylsulfanyl-ethyl)-butyric acid (0.332g) in methanol (10mL) was treated with a solution of Oxone® (1.87g in 10mL of water). After stirring 18 hours at room temperature the reaction mixture was diluted with water (30mL) and evaporated under reduced pressure to remove the methanol. The product was extracted with ethyl acetate. The extracts were washed with saturated aqueous sodium chloride and then dried over magnesium sulfate. The solvent was removed by rotary evaporation and the resulting oil was crystallized from t-butylmethyl ether to give 4-benzenesulfonyl-2-(2-benzenesulfonyl-ethyl)-butyric acid (0.315g).

REFERENCE 5

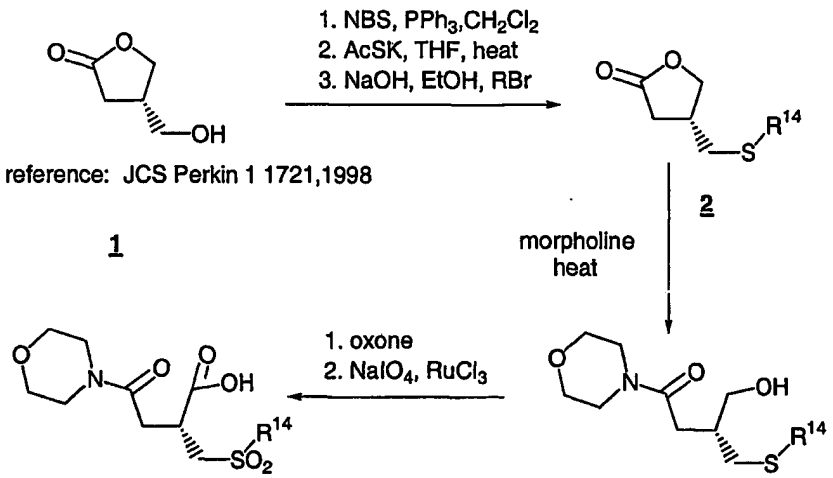
4-Morpholin-4-yl-4-oxo-2-(2-trifluoromethyl-benzylsulfonylmethyl)-butyric acid



A solution of 3-methylene-dihydro-furan-2,5-dione (5.9g, 52.7mmol) in CH_2Cl_2 (200mL) was cooled to 0°C before adding morpholine (4.6mL, 52.7mmol) slowly over 5 minutes. The ice bath was removed and the mixture was stirred at room temperature for 1 hour. The solvent was evaporated under vacuum to 2-Methylene-4-morpholin-4-yl-4-oxo-butyric acid.

A mixture of 2-methylene-4-morpholin-4-yl-4-oxo-butyric acid (2g, 10.03mmol), in DMF (5mL), 2-trifluoromethylbenzyl mercaptan (1.93g, 10.03mmol) and DMAP (122mg, 1.0mmol) was stirred at ambient temperature for 16 hours. Methanol (200mL) and a saturated aqueous solution of Oxone® (20g, 32.5mmol) were added with continued stirring for 2 hours. Methanol was removed under vacuum and the aqueous residue was diluted with 200mL of water. The crystallized product was filtered, washed with water, and dried under vacuum to yield 4-morpholin-4-yl-4-oxo-2-(2-trifluoromethyl-benzylsulfonylmethyl)-butyric acid (0.95g) as a white solid.

Compounds of Formula I in which R^3 is $-CH_2SR^{14}$ (R^{14} is as described in the summary of the invention) can be synthesized by the following reaction protocol:



Compound 1 was prepared as S or R enantiomers using the method described by Crawforth et al. J. Chem. Soc., Perkin Trans. 1, 1721-1725,1998.

Compound 2 was prepared by dissolving compound 1 in methylene chloride with triphenylphosphine (1.1 equivalents) followed by the slow addition of *N*-bromosuccinamide (1.05 equivalents) over a 5 minute period and the reaction was allowed to stir for 3 –8 hours at room temperature. The mixture was then extracted with water and brine, then dried over sodium sulfate. After concentrating the residue was dissolved in ether and a small amount of heptane was added to remove unwanted solids. After filtering and concentration the resulting bromide was used without further purification. This intermediate was dissolved in THF then potassium thioacetate (1.1 equivalents) was added in one portion and the reaction was stirred for 3 to 24 hours at room temperature. The solvent was removed and the residue taken up in ethanol. Sodium hydroxide was added (2.2 equivalents) and the reaction was stirred for 10 to 60 minutes at room temperature. 1 equivalent of a halo-substituted compound (eg. benzyl bromide, isobutyl bromide, cyclopropylmethyl bromide; see other elements from table 2, *supra*) was added with stirring for 6 to 24 hours at room temperature. The ethanol was removed under vacuum and the mixture was diluted with water and made acidic with 4 N HCl (pH=1 to 2). The aqueous layer was extracted with ethyl acetate 3 times and the organic layer was dried over

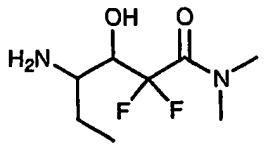
sodium sulfate and concentrated. The product was purified on silica gel using a mixture of ethyl acetate and heptane (gradient 1:4 to 4:1) to give compound 2.

Compound 3 was made by stirring a solution of compound 2 in THF with morpholine (2 equivalents), which was heated, to reflux for 1 to 24 hours. Concentration of the mixture and redissolving in methylene chloride and extraction with diluted HCl removed the excess morpholine. The organic layer was washed with saturated sodium bicarbonate, dried over sodium sulfate and concentrated to dryness. The product was purified on silica gel using a mixture of ethyl acetate and heptane (gradient 1:4 to 4:1) to give compound 3.

Compound 4 was prepared from compound 3 by dissolving in a 1:1 mixture of methanol/water and adding oxone® (approximately 1 equivalent) over a period of 1 to 3 hours until a positive starch-iodine test was maintained. The solvent was removed under vacuum and the residue dissolved in a 1:1:1 mixture of water/acetonitrile/carbon tetrachloride. This was followed by the addition of sodium periodate and ruthenium (III) chloride which was vigorously stirred for 6 to 24 hours at a temperature below 40°C. The reaction was filtered through celite and concentrated to remove acetontrile and carbon tetrachloride. The aqueous layer was extracted with ethyl acetate 3 times and the organic layer dried over sodium sulfate and concentrated. The product was purified on silica gel using a mixture of ethyl acetate and heptane (1:4 to 4:1) to ethyl acetate and methanol (19:1 to 4:1) to give compound 4, which was obtained as R or S enantiomers.

REFERENCE 6

(S)-4-Amino-2,2-difluoro-3-hydroxy-hexanoic acid dimethylamide

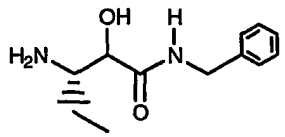


Activated zinc dust (2.16g, 33mmol) was suspended in dry THF (2mL). A mixture of ethyl bromodifluoro acetate (6.5g, 32mmol) and (1S)-(1-formyl-propyl) carbamic acid tert-butyl ester (2g, 10.7mmol), in THF (10mL), was added over 20 minutes while the mixture was sonicated. After complete addition, sonication was continued for a further 30 minutes. The mixture was then diluted with ethyl acetate (200mL) and washed with 1N aqueous $KHSO_4$, brine, dried with magnesium sulfate and evaporated. The crude product was dissolved in ethanol (15mL) and a solution of dimethylamine (40% in water; 2mL) was added. After stirring for 16 hours at ambient temperature, the solvents were evaporated and the product was purified by flash chromatography on silica gel (hexane/ethyl acetate ratio of 3:1) to yield 200mg of colorless oil.

The amide was dissolved in a mixture of TFA/dichloromethyl (1:1; 6mL), stirred for 1 hour and evaporated to dryness. The product, (4S)- 4-amino-2,2-difluoro-3-hydroxy-hexanoic acid dimethylamide, was obtained as the TFA salt and used without further purification.

REFERENCE 7

(S)-3-Amino-2-hydroxy-pentanoic acid benzylamide



(1S)-(2-Cyano-1-ethyl-2-hydroxyethyl)carbamic acid tert-butyl ester (10g, 46.7mmol) was dissolved in 1,4-dioxane (100mL). Anisole (5mL) was added and then concentrated HCl (100mL). The mixture was heated under reflux for 24 hours. The mixture was evaporated to dryness under vacuum and re-dissolved in 100mL water. The solution was washed with ether and then neutralized with saturated aqueous $NaHCO_3$. Di-*tert*-butyl dicarbonate (10g, 46mmol) was added with 1,4-dioxane (200mL), and the mixture was stirred at ambient temperature for 24 hours. The dioxane was removed under vacuum and the remaining aqueous solution was washed with ether. The solution was

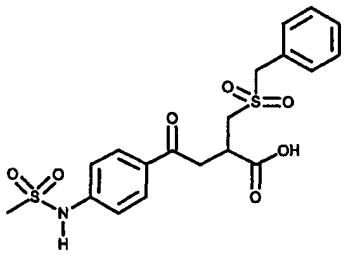
acidified with 1N HCl and extracted with ethyl acetate. The combined organic layers were washed with brine, dried with magnesium sulfate and evaporated to yield 3-tert-Butoxycarbonylamino-2-hydroxy-pentanoic acid (4.5g) as yellowish oil.

3-tert-Butoxycarbonylamino-2-hydroxy-pentanoic acid (300mg, 1.29mmol) was combined with EDC (400mg, 2.1mmol) and HOBt (400mg, 2.6mmol). A solution of benzylamine (0.22mL) and 4-methylmorpholine (0.5mL) in dichloromethyl (4mL) was added in one portion. The mixture was stirred at ambient temperature for 2 hours. After dilution with ethyl acetate (150mL), the solution was washed with 1N aqueous HCl, water, saturated aqueous $NaHCO_3$ solution and brine. The resultant mixture was dried with magnesium sulfate and evaporated under vacuum to yield (S)-3-amino-2-hydroxy-pentanoic acid benzylamide (380mg) as a white solid.

(S)-3-Amino-2-hydroxy-pentanoic acid benzylamide was dissolved in a mixture of TFA/dichloromethyl (1:1; 6mL), stirred for 1 hour and evaporated to dryness. (3S)-3-Amino-2-hydroxy-pentanoic acid benzylamide was obtained as the TFA salt and used without further purification.

REFERENCE 8

4-(4-Methylsulfonylamino-phenyl)-4-oxo-2-benzylsulfonylmethyl -butyric acid



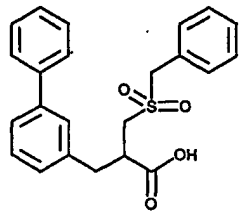
3-Methylene-dihydro-furan-2,5-dione (2g, 17.8mmol) and *N*-phenyl-methylsulfonamide (1.53g, 8.92mmol) were dissolved in anhydrous 1,2-dichloroethane. Aluminum trichloride (4.76g, 35.7mmol) was added and the mixture was stirred at 50°C

for 16 hours. Following dilution with ethyl acetate (400mL), the solution was washed with 1N aqueous HCl, water and brine, dried with magnesium sulfate and evaporated. The product, 4-(4-methylsulfonylamino-phenyl)-2-methylene-4-oxo-butyric acid (1.70g), was crystallized from ethylacetate/hexane.

4-(4-Methylsulfonylamino-phenyl)-2-methylene-4-oxo-butyric acid (800mg, 2.83mmol) was dissolved in DMF (5mL). Benzyl mercaptan (0.5mL, 4.25mmol) and DMAP (200mg, 1.6mmol) were added. The mixture was stirred at ambient temperature for 16 hours. Methanol (200mL) was added and, under vigorous stirring, a saturated aqueous solution of Oxone® (15g, 24.4mmol) was added in one portion. Stirring was continued for 2 hours. Methanol was removed under vacuum and the aqueous residue was diluted with 100mL water. The crystallized product, 4-(4-Methylsulfonylamino-phenyl)-4-oxo-2-benzylsulfonylmethyl-butyric acid (380mg), was filtered, washed with water, and dried under vacuum.

REFERENCE 9

3-Biphenyl-3-yl-2-benzylsulfonylmethyl-propionic acid



Sodium hydride (60% in oil, 1.36g, 34mmol) was dissolved in anhydrous ethanol (50mL) under ice cooling. After the H_2 evolution ceased, diethylmalonate (5.15mL, 34mmol) was added and stirring was continued for 30 minutes at ambient temperature. Then 3-bromobenzyl bromide (4.24g, 16.96mmol) was added and stirring was continued for 2 hours. The reaction mixture was acidified with 1N aqueous HCl and extracted with ethyl acetate (3x150mL). The combined organic layers were washed with brine, dried with

magnesium sulfate and evaporated. The excess diethylmalonate was removed under high vacuum.

The crude product was dissolved in ethanol (50mL) and 1N aqueous NaOH (20mL) was added. After stirring for 16 hours, the mixture was acidified with 1N aqueous HCl and extracted with ethyl acetate. The combined organic layers were washed with brine, dried with magnesium sulfate and evaporated.

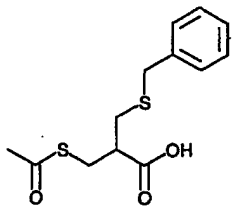
The crude monoacid was dissolved in 1,4-dioxane (20mL). Diethylamine (2.48mL, 24mmol) was added and the solution was cooled to 0°C. Formaldehyde solution (37% in water, 2.44mL) was added and stirring was continued for 24 hours at ambient temperature. After dilution with ethyl acetate (300mL), the solution was washed with water, and brine, dried with magnesium sulfate and evaporated. The crude product, 2-(3-bromo-benzyl)-acrylic acid ethyl ester, was dissolved in ethanol (20mL). Benzylmercaptan (2mL, 17mmol) and triethylamine (4mL) were added. After stirring for 16 hours, 1N aqueous NaOH (50mL) was added and enough 1,4-dioxane to get a homogenous solution. The reaction mixture was warmed to 50°C for 5 hours. All organic solvents were removed under vacuum, and the aqueous residue was acidified to pH 1 with 1N aqueous HCl. The product was extracted with ethyl acetate (3x150mL). The combined organic layers were washed with brine, dried with magnesium sulfate and evaporated. The residue was dissolved in methanol (250mL) and Oxone® (35g) was added. The reaction mixture was stirred at ambient temperature for 2 hours. Methanol was removed under vacuum. The precipitated product was filtered, washed with water, and dried under vacuum. Recrystallization from chloroform gave 3-(3-Bromo-phenyl)-2-benzylsulfonylmethyl-propionic acid (2.43g) as white solid.

3-(3-Bromo-phenyl)-2-benzylsulfonylmethyl-propionic acid (0.5g, 1.26mmol) was dissolved in toluene (20mL) and ethanol (5mL). Tetrakistriphenylphosphine palladium (146mg, 0.126mmol) was added and the mixture was stirred at ambient temperature under nitrogen for 30 minutes. Powdered potassium carbonate (870mg, 6.3mmol) and phenylboronic acid (200mg, 1.64mmol) were added, and the reaction mixture was heated at 75°C for 2 hours. After cooling, the mixture was acidified with 1N aqueous HCl and extracted with ethyl acetate (3x 50mL). The combined organic layers were washed with brine, dried with magnesium sulfate and evaporated. The acid was purified by flash

chromatography on silica gel (ethyl acetate/hexane; 1:1) to yield 3-biphenyl-3-yl-2-benzylsulfonylmethyl-propionic acid (0.40g).

REFERENCE 10

3-Acetylsulfanyl-2-benzylsulfanylmethyl-propionic acid

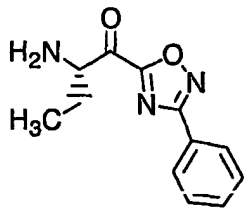


2-Bromomethylacrylic acid (3.00 g, 18.1 mmol) was dissolved in methanol (100mL), cooled on an ice bath and treated with benzyl mercaptan. Aqueous sodium hydroxide (1N, 39.8 mL) was added dropwise and the reaction mixture was allowed to adjust to room temperature with stirring for 23 hours. Methanol was removed by rotary evaporation at reduced pressure and water (100 mL) was added to the residue, which was then washed with ether. The aqueous layer was cooled on ice and acidified to pH 2.5. The precipitated solid was isolated by filtration and dried to give 2-benzylsulfanylmethyl-acrylic acid (3.346 g, 89 %).

A solution of 2-benzylsulfanylmethylacrylic acid (0.208 g) in methylene chloride (2.5 mL) was treated with thiolacetic acid and stirred at room temperature for 72 hours. The reaction mixture was diluted with ethyl acetate (50 mL) and then washed twice with water and once with saturated aqueous sodium chloride. After drying over magnesium sulfate the solvent was removed by rotary evaporation and the residue chromatographed on silica gel eluting with an ethyl acetate/hexane/acetic acid mixture to produce 3-acetylsulfanyl-2-benzylsulfanylmethyl-propionic acid (0.208 g).

REFERENCE 11

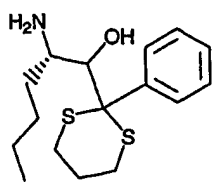
(S)-2-Amino-1-(3-phenyl-[1,2,4]oxadiazol-5-yl)-butan-1-one



3-*tert*-Butoxycarbonylamino-2-hydroxy-pentanoic acid (500mg, 2.14mmol) was combined with EDC (600mg, 3.14mmol), HOBt (600mg, 3.92mmol), and N-hydroxy-benzamidine (292mg, 2.14mmol). Dichloromethyl (10mL) was added and then 4-methylmorpholine (1mL). The mixture was stirred at ambient temperature for 16 hours. After dilution with ethyl acetate (200mL), the solution was washed with water (30mL), saturated aqueous $NaHCO_3$ solution and brine, dried with $MgSO_4$ and evaporated under vacuum. The crude product was dissolved in pyridine (10mL) and heated at 80°C for 15 hours. The pyridine was evaporated under vacuum and the residue was purified by flash chromatography on silica gel (eluent: ethyl acetate) to yield 290mg (0.83mmol). The oxadiazole (145mg, 0.41mmol) was dissolved in CH_2Cl_2 (4mL) and TFA (4mL) was added. After stirring for 1 hour, the mixture was evaporated to dryness to yield (S)-2-Amino-1-(3-phenyl-[1,2,4]oxadiazol-5-yl)-butan-1-one.

REFERENCE 12

2-Amino-1-(2-phenyl-[1,3]dithian-2-yl)-hexan-1-ol.



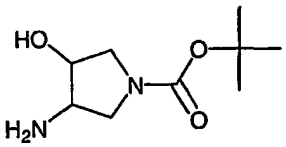
2-phenyl-1,3-dithiane (Aldrich) (3.79g; 19.3mmol) was mixed with dry distilled

THF (20mL) under a nitrogen atmosphere. The solution was cooled to –60 °C and n-butyl lithium (1.6M in pentane, 1.56 mmol, 9.74mL) was added slowly by syringe. The reaction mixture was warmed to –20 °C and held at that temperature for 30 minutes, and then held at –10 °C for 15 minutes. The yellow solution was cooled to –78 °C and (1-Formyl-pentyl)-carbamic acid *tert*-butyl ester (1.6 g, 1.4 mmol, in 5 ml THF) was added rapidly (over 20 seconds) and 60 seconds later a mixture of 2mL acetic acid and 5mL THF was added rapidly. After warming to 23°C the solution was concentrated at reduced pressure. Excess 2-phenyl-1,3-dithiane was removed by its crystallization away from the desired product using a minimum of ethyl acetate in hexane. The mother liquors were concentrated and chromatographed using a hexane-ethyl acetate gradient to afford 1.7 g of {1-[Hydroxy-(2-phenyl-[1,3]dithian-2-yl)-methyl]-pentyl}-carbamic acid *tert*-butyl ester. (56% yield).

To {1-[Hydroxy-(2-phenyl-[1,3]dithian-2-yl)-methyl]-pentyl}-carbamic acid *tert*-butyl ester (608 mg, 1.47 mmol) in 2.7mL dioxane at 10 °C was added hydrochloric acid (2.7mL, 4M in dioxane). The solution was warmed to 23°C. After 3 hours the solution was diluted with 5 ml toluene and concentrated under reduced pressure. The gummy solid was washed with diethyl ether resulting in the hydrochloride salt of 2-amino-1-(2-phenyl-[1,3]dithian-2-yl)-hexan-1-ol, 414 mg, 82% as a free flowing solid after removal of excess ether under reduced pressure.

REFERENCE 13

3-Amino-4-hydroxo-pyrrolidine-1-carboxylic acid tert-butyl ester

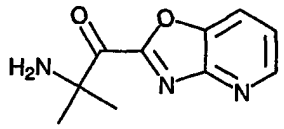


6-Oxa-3-aza-bicyclo[3.1.0]hexane-3-carboxylic acid tert-butyl ester (12.1g, 65.3mmol) was dissolved in a 8:1 methanol/water mixture (108mL). Ammonium chloride

(15g) and sodium azide (21.4g, 329mmol) was added and the mixture was heated at 60°C overnight. After dilution with ether (500mL), the mixture was washed with saturated aqueous $NaHCO_3$ (200mL) and brine (200mL), dried with $MgSO_4$ and evaporated under vacuum. The crude product was dissolved in methanol (200mL). 10% Palladium on activated carbon (1.5g) was added and the mixture was stirred at ambient temperature under a hydrogen atmosphere until TLC analysis showed the disappearance of the starting material. The mixture was filtered through a pad of Celite and evaporated to dryness under vacuum. The product was purified by flash chromatography on silica gel. Eluent: 5% methanol in ethyl acetate to 20% methanol, 3% triethylamine in ethyl acetate. Yield: 4.3g of 3-amino-4-hydroxy-pyrrolidine-1-carboxylic acid tert-butyl ester as yellowish solid.

REFERENCE 14

2-Amino-2-methyl-1-oxazolo[4,5-b]pyridin-2-yl-propan-1-one



2-amino-2-methyl-1-propanol (17.8 g, 200 mmol) was dissolved in a mixture of water and 100 ml dioxane and cooled to 0°C. NaOH (8g, 200mmol) and di-t-butyl-dicarbonate (52.4g, 240mmol) were added and the reaction was allowed to warm to room temperature with stirring for 2 hours. After removing the dioxane, the residue was extracted with EtOAc, washed with brine, dried with anhydrous $MgSO_4$, filtered and concentrated to yield 35g of product.

A solution of oxylyl chloride (15.24g, 120mmol) in 200ml of $MeCl_2$ was stirred and cooled to –60°C followed by the drop wise addition of dimethylsulfoxide (19.7g, 252mmol) in 60ml of $MeCl_2$. After 10 minutes, a solution of 2-bocamino-2-methyl-1-propanol (18.9g, 100mmol) in 60ml of $MeCl_2$ was added drop wise at –70°C. The reaction mixture was allowed to warm to –40°C for 10 minutes followed by cooling to –70°C before the addition of a solution of triethylamine (28.28g, 280mmol) in 60 ml of $MeCl_2$. The

reaction mixture was allowed to warm to room temperature over a two-hour period and 40ml of saturated sodium dihydrogen phosphate was added. The organic layer was washed with brine and dried over $MgSO_4$. The solvent was removed to yield 17.3 g of aldehyde.

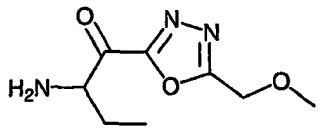
A mixture of 2-amino-3-hydroxy pyridine (11g, 100mmol), triethylorthoformate (80ml) and p-toluenesulfonic acid (61mg) was heated at 140°C for 8 hours. Excess triethylorthoformate was removed under vacuum. The product was crystallized from ethyl acetate to yield 9g of pyridyloxazole; H^1 NMR (DMSO-δ): 9.26 (1H, s), 8.78 (1H, d), 8.45 (1H, d), 7.7(1H, dd); MS: 120.8 (M+1).

To a stirred solution of the pyridyloxazole (2.4 g, 20mmol) in THF (100ml) was added n-BuLi (1.6M solution in 12.5ml of hexane) drop wise under N_2 at –78°C. After 1 hour, $MgBr.Et_2O$ (5.16g, 20mmol) was added and the reaction mixture was allowed to warm to –45°C for 1 hour before being treated with 2-boc-amino-2-methyl-propanyl-aldehyde (2.24g, 12mmol) in THF (20ml). The reaction mixture was stirred for 1 hour, quenched with saturated NH_4Cl, and extracted with ethyl acetate. The organic layer was washed with brine, dried with $MgSO_4$ and concentrated. The residue was purified by silica gel column chromatography to yield 2-boc-amino-2-methyl-1-(5-pyridyloxazole-2-yl)-1-propanol (1.18g); H^1 NMR (DMSO-δ): 8.5(1H, d,d, J=1.46Hz, J=4.94Hz), 8.14(1H, d,d, J1.49Hz, J=8.16Hz), 7.41(1H, d,d, J=4.7Hz, J=8.18Hz), 7.1-6.8(1H, d, d), 6.53(1H, br, NH), 6.24, 6.22(1H, s,s, OH), 5.23, 5.21(1H, s,s, , 1.37(3H, s, CH3), 1.33(9H, s, 3xCH3), 1.22(3H, s, CH3); MS: 308.2 (M+1).

2-Boc-amino-2-methyl-1-(5-pyridyloxazole-2-yl)-1-propanol (156mg, 0.508mmol) and $MeCl_2$ (5ml) were mixed and TFA (0.5ml) was added at room temperature. After stirring for 1 hour, the solvent and excess TFA were removed under vacuum to produce 2-amino-2-methyl-1-oxazolo[4,5-b]pyridin-2-yl-propan-1-one TFA salt (165mg).

REFERENCE 15

2-Amino-1-(5-methoxymethyl-[1,3,4]oxadiazol-2-yl)-butan-1-one



(S)-(+)-2-amino-1-butanol (50g, 561mmol) in 200ml of water and 200ml dioxane was cooled to 0°C and mixed with NaOH (26.9g, 673mmol) and di-t-butyl-dicarbonate (146.96 g, 673mmol). After the addition, the reaction was allowed to warm to room temperature. The reaction mixture was stirred for 2 hours. After removing the dioxane, the residue was extracted with EtOAc, then washed with brine and dried with anhydrous $MgSO_4$, filtered and concentrated. Without further purification, the crude product (120g) was used for next step reaction.

A solution of oxylyl chloride (40.39 g, 265mmol) in 700ml of $MeCl_2$ was stirred and cooled to –60°C. Dimethylsulfoxide (51.7 g, 663mmol) in 100 ml of $MeCl_2$ was added drop wise. After 10 minutes a solution of (S)-2-boc-amino-1-butanol (50 g, 265 mmol) in 100ml of $MeCl_2$ was added drop wise at –70°C. The reaction mixture was allowed to warm to –40°C for 10 minutes and then cooled to –70°C again. A solution of triethylamine (74.9 g, 742mmol) in 100 ml of $MeCl_2$ was added. The reaction mixture was allowed to warm to room temperature over 2 hours. 100mls of saturated sodium dihydrogen phosphate was added, and then the organic layer was washed with brine and dried over $MgSO_4$. The solvent was removed to yield 45g of (1-formyl-propyl)-carbamic acid tert-butyl ester; H^1 NMR (DMSO-δ): 9.4(1H, s), 7.29(1H, br.), 3.72(1H, m), 1.69(2H, m), 1.4-1.2(9H, s), 0.86(3H, t).

A mixture of methyl methoxyacetate (52g, 500mmol), hydrazine hydrate (30ml) was heated to reflux for 8 hours. Excess hydrazine and water were removed under vacuum. The residue was extracted with n-butanol, dried with Na_2SO_4. Excess n-butanol was removed to yield 45g of hydrazide.

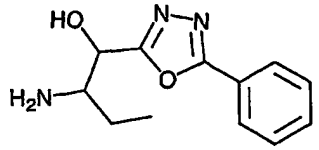
A mixture of above hydrazide (45g), triethylorthoformate (146ml) and p-toluenesulfonic acid (61mg) was heated at 140°C for 8 hours. Excess triethylorthoformate was removed under vacuum. The product was purified by silica gel column chromatography to yield 4.6g of 2-methoxymethyl-1,3,4-oxadiazole; H^1 NMR (DMSO-δ): 9.21(1H, s), 4.63(2H, s), 3.27(3H, s).

To a stirred solution of 2-methoxymethyl-1,3,4-oxadiazole (4.6 g, 40mmol) in THF (100ml) was added n-BuLi (1.6M solution in 25.2ml of hexane) drop wise under N_2 at –78°C. After 1 hour, MgBr.Et_2O (10.4g, 40.3mmol) was added and the reaction mixture was allowed to warm to –45°C for 1 hour before being treated with 2-boc-amino-propanyl aldehyde (5.28g, 28.25mmol) in THF (20ml). The reaction mixture was stirred for 1 hour, quenched with saturated NH_4Cl, and extracted with ethyl acetate. The organic layer was washed with brine, dried with $MgSO_4$ and concentrated. The residue was purified by silica gel column chromatography to yield 2-boc-amino-1-(5-methoxymethyl-1,3,4-oxadiazole-2-yl)-1-propanol (500mg); H^1 NMR (DMSO-δ): 6.7(1/2H, d, NH, diastereomeric), 6.5(1/2H, d, NH, diastereomeric), 6.2(1/2H, d, OH, diastereomeric), 6.0(1/2H, d, OH, diastereomeric), 4.83-4.79(1H, m), 4.55(2H, s), 4.05-3.5(1H, m), 3.31(3H, s), 1.9-1.4(2H, m), 1.4-1.2(9H, m), 0.85-0.81(3H, m); MS: 300.4(M-1), 302.4(M+1).

2-Boc-amino-1-(5-methoxymethyl-1,3,4-oxadiazole-2-yl)-1-propanol(500mg, 1.66mmol), and $MeCl_2$ (5ml) were mixed and TFA (0.5ml) was added at room temperature. After stirring for 1 hour, the solvent and excess TFA were removed under vacuum to produce 2-amino-1-(5-methoxymethyl-[1,3,4]oxadiazol-2-yl)-butan-1-one TFA salt (340mg).

REFERENCE 16

2-Amino-1-(5-phenyl-[1,3,4]oxadiazol-2-yl)-1-butanol



A mixture of the benzylhydrazide (22.5g, 165mmol), triethylorthoformide (150ml) and p-toluenesulfonic acid (300mg) was heated at 120°C for 12 hours. Excess triethylorthoformide was removed under vacuum and the residue was purified by silica gel column chromatography to produce oxadiazole (14.5g); H^1 NMR (DMSO-δ): 9.34 (1H, s),

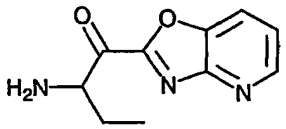
8.05-7.98 (2H, m), 7.68-7.55 (3H, m); MS: 147.4 (M+1).

To a stirred solution of the oxadiazole (10g, 68.5mmol) in THF (100ml) was added n-BuLi (1.6M solution in 42.8ml of hexane) drop wise under N_2 at –78°C. After 1 hour, $MgBr.Et_2O$ (17.69g, 68.5mmol) was added and the reaction mixture was allowed to warm to –45°C for 1 hour before being treated with 2-boc-amino-butyl-aldehyde (7.8g, 41mmol) in THF (20ml). The reaction mixture was stirred for 1 hour, quenched with saturated NH_4Cl, and extracted with ethyl acetate. The organic layer was washed with brine, dried with $MgSO_4$ and concentrated. The residue was purified by silica gel column chromatography to yield 2-(2-boc-amino-1-hydroxydutyl)-5-benzyl-1,3,4-oxadiazole (9.7g); H^1 NMR (DMSO-δ): 8-7.9(2H, m), 7.8-7.7(3H, m), 6.8-6.6(1H, d,d, NH, diastereomeric), 6.4-6.1(1H, d,d, OH, diastereomeric), 5-4.4(1H, m), 1.9-1.3(2H, m), 1.3-1.1(9H, s, s), 0.84(3H, t); MS: 334.5(M+1).

2-(2-Boc-amino-1-hydroxybutyl)-5-benzyl-1,3,4-oxadiazole (505mg, 1.5mmol) and $MeCl_2$ (5ml) were mixed and TFA (1ml) was added at room temperature. After stirring for 1 hour, the solvent and excess TFA were removed under vacuum to produce 530mg of 2-amino-1-(5-phenyl-[1,3,4]oxadiazol-2-yl)-1-butanol TFA salt.

REFERENCE 17

2-Amino-1-oxazolo[4,5-b]pyridin-2-yl-butan-1-one



A mixture of 2-amino-3-hydroxy pyridine (25g, 227mmol), triethylorthoformate (75ml) and p-toluenesulfonic acid (61mg) was heated at 140°C for 8 hours. Excess triethylorthoformate was removed under vacuum. The product was crystallized from ethyl acetate to yield 22.5g of pyridyloxazole; H^1 NMR (DMSO-δ): 9.26 (1H, s), 8.78 (1H, d), 8.45 (1H, d), 7.7(1H, dd); MS: 120.8 (M+1).

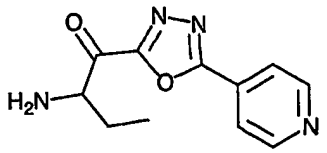
Pyridyloxazole (600 mg, 5 mmol) in 30 ml THF was cooled to 0°C before the addition of isopropanyl magnesium chloride (2M in THF, 2.5 ml, 5 mmol). After stirring for 1 hour at 0°C, the aldehyde (573 mg, 3 mmol) in 20 ml THF was added. The ice bath was removed and the reaction allowed to warm to room temperature. The reaction mixture was stirred for 2 hours and quenched with saturated ammonium chloride solution. Excess THF was removed and the residue was extracted with EtOAc, washed with brine, dried with anhydrous $MgSO_4$, filtered and concentrated. The crude residue was purified by chromatography to yield 383 mg product; H^1 NMR (DMSO-δ): 8.42(1H, m), 8.18(1H, m), 7.3(1H, m), 6.8, 6.6(1H, dd, d, OH, diastereomeric), 6.3, 6.02(1H, d, d, NH, diastereomeric), 4.82, 4.5(1H, m, m, diastereomeric), 1.8-1.3(2H, m), 1.2, 1.05(9H, s,s, diastereomeric), 0.89(3H, m); MS: 306.2(M-1), 308.6(M+1).

To a stirred solution of the pyridyloxazole (12g, 100mmol) in THF (300ml) was added n-BuLi (1.6M solution in 62.5ml of hexane) drop wise under N_2 at –78°C. After 1 hour, $MgBr.Et_2O$ (25.8g, 100mmol) was added and the reaction mixture was allowed to warm to –45°C for 1 hour before being treated with 2-boc-amino-butyl-aldehyde (11.46g, 60mmol) in THF (50ml). The reaction mixture was stirred for 1 hour, quenched with saturated NH_4Cl, and extracted with ethyl acetate. The organic layer was washed with brine, dried with $MgSO_4$ and concentrated. The residue was purified by silica gel column chromatography to yield 2-boc-amino-1-(5-pyridyloxazole-2-yl)-1-butanol (14.1g).

2-Boc-amino-1-(5-pyridyloxazole-2-yl)-1-butanol (311mg, 1mmol) and $MeCl_2$ (5ml) were mixed and TFA (1ml) was added at room temperature. After stirring for 1 hour, the solvent and excess TFA were removed under vacuum to produce 355mg of 2-amino-1-oxazolo[4,5-b]pyridin-2-yl-butan-1-one TFA salt.

REFERENCE 18

2-Amino-1-(5-pyridin-4-yl-[1,3,4]oxadiazol-2-yl)-butan-1-one



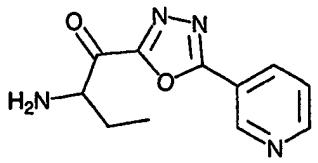
A mixture of the isonicotinic hydrazide (13.7g, 100mmol), triethylorthoformate (60ml) and p-toluenesulfonic acid (30mg) was heated at 130°C for 12 hours. Excess triethylorthoformate was removed under vacuum. The product was crystallized from ethyl acetate to yield 14.8 g; H^1 NMR (DMSO-δ): 9.46 (1H, s), 8.8 (2H, dd), 7.9 (2H, dd).

To a stirred solution of the oxadiazole (11.5g, 78.2mmol) in THF (300ml) was added 5ml HMPA and n-BuLi (1.6M solution in 48.9ml of hexane) drop wise under N_2 at –78°C. After 1 hour, $MgBr.Et_2O$ (20.2g, 78.2mmol) was added and the reaction mixture was allowed to warm to –45°C for 1 hour before being treated with 2-boc-amino-butylldehyde (9.7g, 50.8mmol) in THF (50ml). The reaction mixture was stirred for 1 hour, quenched with saturated NH_4Cl, and extracted with ethyl acetate. The organic layer was washed with brine, dried with $MgSO_4$ and concentrated. The residue was purified with silica gel column chromatography to yield 2-bocamino-1-(5-pyridin-4-yl-[1,3,4]oxadiazol-2-yl)-butan-1-ol (3.5g); H^1 NMR (DMSO-δ): 8.85-8.8(2H, m), 7.95-7.8(2H, m), 6.66(1H, d,), 6.19(1H, d), 4.96(1H, t), 3.75-3.6(1H, m), 1.72-1.6(1H, m), 1.5-1.35(1H, m), 1.27(9H, s), 0.87(3H, t); MS: 333.2 (M-1), 335.4 (M+1).

2-Bocamino-1-(5-pyridin-4-yl-[1,3,4]oxadiazol-2-yl)-butan-1-ol (334mg, 1mmol) and $MeCl_2$ (5ml) were mixed and TFA (0.5ml) was added at room temperature. After stirring for 1 hour, the solvent and excess TFA were removed under vacuum to produce 350mg of 2-amino-1-(5-pyridin-4-yl-[1,3,4]oxadiazol-2-yl)-butan-1-one TFA salt.

REFERENCE 19

2-Amino-1-(5-pyridin-3-yl-[1,3,4]oxadiazol-2-yl)-butan-1-one

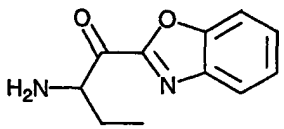


To a stirred solution of the 3-[1,3,4] oxadiazol-2-yl-pyridine (5g, 34mmol) in THF (100ml) was added 5ml HMPA and n-BuLi (1.6M solution in hexane, 21.25ml) drop wise under N_2 at –78°C. After 1 hour, $MgBr.Et_2O$ (8.77g, 34mmol) was added and the reaction mixture was allowed to warm to –45°C for 1 hour before being treated with 2-boc-amino-butylldehyde (4.22g, 22.1mmol) in THF (20ml). The reaction mixture was stirred for 1 hour, quenched with saturated NH_4Cl, and extracted with ethyl acetate. The organic layer was washed with brine, dried with $MgSO_4$ and concentrated. The residue was purified with silica gel column chromatography to yield 2-boc-amino-1-(5-pyridin-3-yl-[1,3,4]oxadiazol-2-yl)-butan-1-ol (1.5g); H^1 NMR (DMSO-d): 9.2-9.1(1H, d), 8.82-8.76(1H, m), 8.4-8.3(1H, m), 7.68-7.6(1H, m), 6.78, 6.65(1H, d d, NH, diastereomeric), 6.38, 6.16(1H, d,d, OH, diastereomeric), 3.8-3.6(1H, m), 1.9-1.2(2H, m), 1.3, 1.1(9H, s,s,), 0.84(3H, t); MS: 331.2 (M-1).

2-Boc-amino-1-(5-pyridin-3-yl-[1,3,4]oxadiazol-2-yl)-butan-1-ol (167mg, 0.5mmol) and $MeCl_2$ (5ml) were mixed and TFA (0.5ml) was added at room temperature. After stirring for 1 hour, the solvent and excess TFA were removed under vacuum to produce 180mg of 2-amino-1-(5-pyridin-3-yl-[1,3,4]oxadiazol-2-yl)-butan-1-one TFA salt.

REFERENCE 20

2-Amino-1-benzooxazol-2-yl-butan-1-one

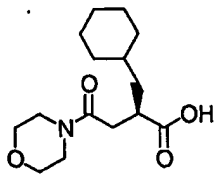


Benzoxazole (600 mg, 5 mmol) in 20 ml THF was cooled to -5°C and isopropyl magnesium chloride (2 M in THF, 2.5 ml, 5 mmol) was added. After stirring for 1 hour at -5°C, the aldehyde (561 mg, 3 mmol), prepared as in reference 15, in 10 ml THF was added. The reaction was allowed to warm to room temperature with stirring for 2 hours. The reaction was quenched with saturated ammonium chloride solution, excess THF solvent removed. The residue was extracted with EtOAc, washed with brine, dried with anhydrous $MgSO_4$, filtered and concentrated. The crude residue was purified by chromatograph to yield 688 mg product (75%); LC-MS: 305.2 (M-1), 307.0 (M+1); H^1NMR (DMSO-d_6): 7.72-7.6 (2H, m), 7.38-7.28 (2H, m), 6.7 (d)-6.52(d) (1H, NH, diastereomeric), 6.12(d)-5.92 (d) (1H, OH, diastereomeric), 4.81(dd)-4.57(dd) (1H, CH-OH), 3.74 (1H, m), 1.9-1.6 (1H, m), 1.6-1.3 (1H, m), 1.25(s)-1.1(s) (9H, diastereomeric), 0.85 (3H, t).

[1-(Benzooxazol-2-yl-hydroxy-methyl)-propyl]-carbamic acid *tert*-butyl ester (275mg, 0.89mmol) and $MeCl_2$ (5ml) were mixed and TFA (1ml) was added at room temperature. After stirring for 1 hour, the solvent and excess TFA were removed under vacuum to produce 260mg of 2-amino-1-benzooxazol-2-yl-butan-1-one TFA salt.

REFERENCE 21

2-Cyclohexylmethyl-4-morpholin-4-yl-4-oxo-butyric acid

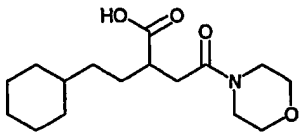


A 0.05 M solution of 1-(4-benzyl-2-oxo-oxazolidin-3-yl)-2-cyclohexylmethyl-4-morpholin-4-yl-butane-1,4-dione (1g) in 3:1 –THF/H_2O was treated at 0°C with 8 equivalents of 30% H_2O_2 followed by 2.0 equivalents of LiOH. The resulting mixture was stirred at 0-25°C until the substrate had been consumed (approximately 1 hour). The excess peroxide was quenched at 0°C with a 10% excess of 1.5 N aqueous Na_2SO_3. After

buffering to pH 9-10 with aqueous $NaHCO_3$ and evaporation of the THF, the oxazolidone chiral auxiliary was recovered by $MeCl_2$ extraction. The carboxylic acid was isolated by EtOAc extraction of the acidified (pH 1-2) aqueous phase, then recrystallized from EtOAc and hexane to yield 0.58g of 2-cyclohexylmethyl-4-morpholin-4-yl-4-oxo-butyric acid; H^1 NMR (DMSO-δ): 12(1H, s, COOH), 3.6-3.3(8H, m), 2.8-2.3(3H, m), 1.8-1.1(11H, m), 0.9-0.7(2H, m); MS: 282.2(M-1), 284.1 (M+1).

REFERENCE 22

2-(2-Cyclohexyl-ethyl)-4-morpholin-4-yl-4-oxo-butyric acid



(S)-(-)-4-Benzyl-2-oxazolidinone (5g, 28.2mmol) was dissolved in THF (100mL) and cooled to –78°C under nitrogen. A 2.5M solution of n-butyllithium in hexane (12.4mL) was added with a syringe and the mixture was stirred for 30min. 4-Cyclohexyl-butyryl chloride (5.85g, 31mmol) was added at –78°C. The mixture was allowed to warm to 0°C over two hours. 1N HCl (50mL) was added and the product was extracted with ethyl acetate (3x100mL). The combined organic layers were washed with saturated aqueous $NaHCO_3$ (200mL) and brine (200mL), dried with $MgSO_4$ and evaporated under vacuum. The product was recrystallized from hexane/ether and obtained as a white solid (5.6g).

A solution of diisopropylamine (1.92mL, 13.68mmol) in dry THF (50mL) was cooled to –20°C. A 2.5M solution of n-butyllithium in hexane (4.4mL) was added with a syringe. The mixture was stirred for 30min and then cooled to –78°C. A solution of 4-benzyl-3-(4-cyclohexyl-butyryl)-oxazolidin-2-one (3g, 9.12mmol) in THF (10mL) was added slowly over 3min. Stirring was continued for 30min, then a solution of 2-Bromo-1-morpholin-4-yl-ethanone (2.28g, 10.94mmol) in THF (4mL) was added over 3min. The mixture was allowed to come to room temperature over 5h. 1N HCl (50mL) was added and

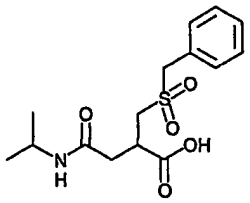
the product was extracted with ethyl acetate (3x100mL). The combined organic layers were washed with saturated aqueous $NaHCO_3$ (200mL) and brine (200mL), dried with $MgSO_4$ and evaporated under vacuum. The product (1-(4-benzyl-2-oxo-oxazolidin-3-yl)-2-(2-cyclohexyl-ethyl)-4-morpholin-4-yl-butane-1,4-dione) was obtained after purification by flash chromatography as a single diastereomer (2.5g). ^1H NMR: ($CDCl_3$) 7.35-7.22 (m, 5H), 4.69-4.62 (m, 1H), 4.28-4.10 (m, 3H), 3.76-3.46 (m, 8H), 3.37 (d, J=13.6Hz, 1H), 2.91 (ddd, J=16.4Hz, J=13Hz, J=3Hz, 1H), 2.76 (ddd, J=13.5Hz, J=11Hz, J=3Hz, 1H), 2.51 (dt, J=13.6Hz, J=3Hz, 1H), 1.76-0.80 (m, 15H). MS: $(M+H)^+$ 457.

1-(4-Benzyl-2-oxo-oxazolidin-3-yl)-2-(2-cyclohexyl-ethyl)-4-morpholin-4-yl-butane-1,4-dione (2.5g, 5.48mmol) was dissolved in a 3:1-THF/H_2O mixture (50mL) and cooled to 0°C. H_2O_2 (5mL) was added followed by lithium hydroxyde monohydrate (462mg, 11mmol). The mixture was stirred at 0°C for 30min. Excess peroxide was quenched with 1.5N Na_2SO_3 solution and the THF was evaporated under vacuum. The chiral auxiliary was removed by extraction with diethyl ether. After acidification to pH 1 the product was isolated by extraction with ethyl acetate. The combined organic layers were washed with saturated aqueous $NaHCO_3$ (200mL) and brine (200mL), dried with $MgSO_4$ and evaporated under vacuum. The crude acid ((2R)-2-(2-Cyclohexyl-ethyl)-4-morpholin-4-yl-4-oxo-butyric acid) was used for coupling (EDC) and oxidation (Dess-Martin) as described in the examples, *infra*.

(2R)-1-((4S)-4-Benzyl-2-oxo-oxazolidin-3-yl)-2-cyclohexylmethyl-4-morpholin-4-yl-butane-1,4-dione was prepared by the same procedure as described for reference 22. 4-Cyclohexyl-butyryl chloride was substituted by 3-cyclohexyl-propionyl chloride. ^1H NMR: (DMSO) 7.35-7.22 (m, 5H), 4.63-4.56 (m, 1H), 4.28 (t, J=8.5Hz, 1H), 4.17-4.06 (m, 2H), 3.70-3.35 (m, 8H), 2.94 (d, J=13.2Hz, 1H), 2.82 (dd, J=13.2Hz, J=8Hz, 1H), 2.72 (dd, J=16Hz, J=10.4Hz, 1H), 2.51 (dd, J=16Hz, J=3.2Hz, 1H), 1.75-0.75 (m, 13H); MS: $(M+H)^+$ 443.

REFERENCE 23

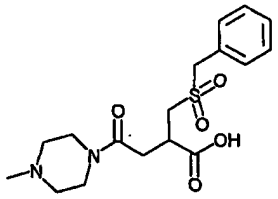
N-Isopropyl-2-benzylsulfonylmethyl-succinamic acid



To a stirring mixture of itacconic anhydride (1.1209g, 10mmol) in 10 ml of methylene chloride at 0°C was added drop wise isopropyl amine (0.85ml, 10mmol). The reaction was stirred at room temperature for 1 hour and the solvent was removed under reduced pressure to give 2-(isopropylcarbamoyl-methyl)-acrylic acid. The residue was dissolved in 10 ml of DMF, then benzyl mercaptan (1.17g, 10.0mmol) and DMAP (122mg, 1mmol) were added and the reaction was stirred at room temperature for overnight. The mixture containing 2-benzylsulfanylmethyl-*N*-isopropyl-succinamic acid was cooled to 0°C and oxone® (4.9182g, 8mmol) in 20 ml of water was added and stirred for 2 hours at room temperature. More oxone® was added and the reaction was stirred at room temperature for 18 hours. The reaction was filtered and the white solid was washed with water, ether and dried under high vacuum to give 1.0 grams of *N*-isopropyl-2-benzylsulfonylmethyl-succinamic acid, which was used without further purification; LCMS retention time 2:32minutes: MS+1 (328.1).

REFERENCE 24

4-(4-Methyl-piperazin-1-yl)-4-oxo-2-benzylsulfonylmethyl-butyric acid

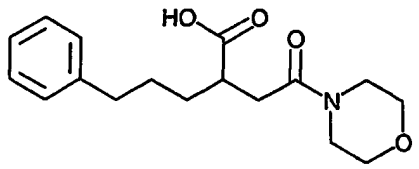


To a stirring mixture of itacconic anhydride 1.1209g, 10mmol) in 10 ml of methylene chloride at 0°C was added drop wise methyl piperizine (1.0g, 10mmol). The

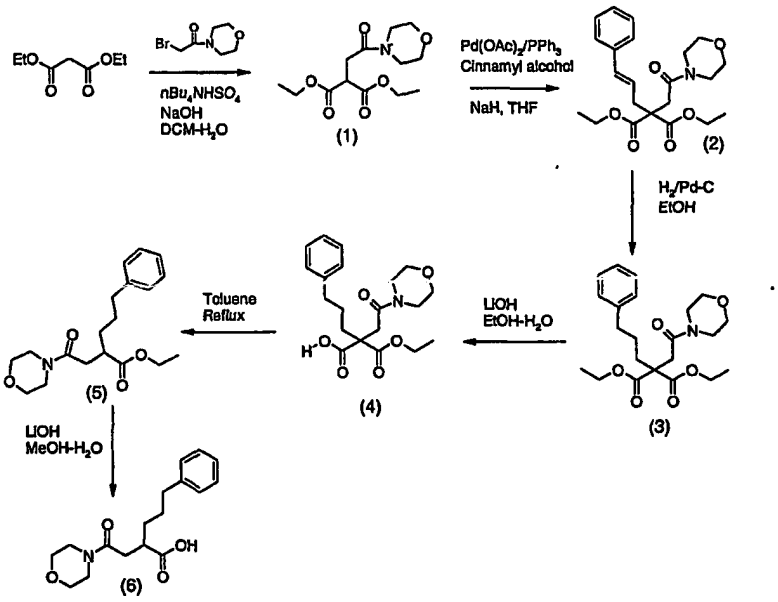
reaction was stirred at room temperature for 1 hour and the solvent was removed under reduced pressure to give compound 2-[2-(4-methyl-piperazin-1-yl)-2-oxo-ethyl]-acrylic acid. The residue was dissolved in 10 ml of DMF, then benzyl mercaptan (1.17g, 10.0mmol) and DMAP (122mg, 1mmol) were added and heated to 50-60°C until reaction turned clear then the reaction was stirred at room temperature for overnight. Another 0.59 ml of benzyl mercapton (5mmol) was added and the reaction was stirred overnight at room temperature. The mixture containing compound 2-benzylsulfanylmethyl-4-(4-methyl-piperazin-1-yl)-4-oxo-butyric acid was cooled to 0°C and oxone® (6.1378g, 10mmol) in 20 ml of water was added and stirred for overnight at room temperature. More oxone® was added and the reaction was stirred at room temperature for 2 hours. The reaction was filtered and the product was in the aqueous phase and was purified on HPLC to give 0.2477 gram of pure 4-(4-methyl-piperazin-1-yl)-4-oxo-2-benzylsulfonylmethyl-butyric acid; LCMS retention time: 1.72 minutes; M+1 (369.3).

REFERENCE 25

2-(2-Morpholin-4-yl-2-oxo-ethyl)-5-phenyl-pentanoic acid



Reference 25 was synthesized as described in the following reaction protocol:



2-(2-Morpholin-4-yl-2-oxo-ethyl)-malonic acid diethyl ester (1)

To a solution of n-tetra butyl ammonium hydrogen sulfate (1.18g, 3.48 mmol) and NaOH (560 mg, 13.9 mmol) in water (8 ml) was added a solution of 4-(2-bromoacetyl morpholine) (1.45g, 6.97 mmol) and diethyl malonate (1.34g, 8.36 mmol) in DCM (8 ml). The mixture was stirred at room temperature for 3 hours, diluted with water (30 ml) and extracted with DCM (2x30 ml). The organic layer was dried ($MgSO_4$) and concentrated in vacuum. The residue was purified by chromatography (silica) eluting with 1:2 v/v ethyl acetate – heptane to give 2-(2-morpholin-4-yl-2-oxo-ethyl)-malonic acid diethyl ester as a colorless oil (1.19 g, 59%); ^{1}H NMR ($CDCl_3$) 4.25 (m, 4H), 4.0 (t, J=7.2Hz, 1H), 3.8-3.45 (m, 8H), 3.0 (d, J=7.4Hz, 2H), 1.3 (t, J=7.1Hz, 6H).

2-(2-Morpholin-4-yl-2-oxo-ethyl)-2-(3-phenyl-allyl)-malonic acid diethyl ester (2)

To a mixture of $Pd(OAc)_2$ (17.5 mg, 0.078 mmol) and PPh_3 (40.9 mg, 0.156mmol) in dry THF (2ml) under N_2, cinnamyl alcohol (105.1 mg, 0.78 mmol) was added followed

by a solution of 2-(2-morpholin-4-yl-2-oxo-ethyl)-malonic acid diethyl ester (250 mg, 0.87 mmol) and NaH (17.4 mg, 0.43 mmol) in dry THF (3 ml). BF_3 (1M in THF, 1ml, 1 mmol) was then added and the yellow solution was stirred at room temperature for 6.5 hours. The mixture was diluted with ethyl acetate (50 ml) and washed with 1N HCl (10 ml) and brine (2 x 20 ml). The organic layer was dried ($MgSO_4$), concentrated in vacuum and purified by chromatography eluting with 1:1 v/v ethyl acetate – heptane mixture to give 2-(2-morpholin-4-yl-2-oxo-ethyl)-2-(3-phenyl-allyl)-malonic acid diethyl ester as a thick, yellow oil (266.5 mg, 85%); ^{1}H NMR ($CDCl_3$) 7.25 (m, 5H), 6.40 (d, J=15.6Hz, 1H), 6.1 (dt, J=15.8, 7.7Hz), 4.2 (q, J=7.1Hz, 4H), 3.6 (m, 6H), 3.45 (m, 2H), 3.05 (d, J=7.6Hz, 2H), 3.0 (s, 2H), 1.25 (t, J=7.1Hz, 6H). MS: 404 (MH^+)

2-(2-Morpholin-4-yl-2-oxo-ethyl)-2-(3-phenyl-propyl)-malonic acid diethyl ester (3)

A solution of 2-(2-morpholin-4-yl-2-oxo-ethyl)-2-(3-phenyl-allyl)-malonic acid diethyl ester (257 mg, 0.637 mmol) in EtOH (15 ml) was hydrogenated over Pd/C at 55 Psi for 7.5 hrs. The catalyst filtered off over a pad of Celite and the filtrate evaporated under vacuum to give 2-(2-morpholin-4-yl-2-oxo-ethyl)-2-(3-phenyl-propyl)-malonic acid diethyl ester as a light yellow oil (260 mg); ^{1}H NMR ($CDCl_3$) 7.4-7.1 (m, 5H), 4.20 (q, J=7.1Hz, 4H), 3.7-3.4 (m, 8H), 3.0 (s, 2H), 2.6 (t, J=7.6Hz, 2H), 2.2 (m, 2H), 2.55 (m, 2H), 1.20 (t, J=7.1Hz, 6H). MS: 406 (MH^+).

2-(2-Morpholin-4-yl-2-oxo-ethyl)-2-(3-phenyl-propyl)-malonic acid monoethyl ester (4)

To a solution of 2-(2-morpholin-4-yl-2-oxo-ethyl)-2-(3-phenyl-propyl)-malonic acid diethyl ester (934 mg, 2.3 mmol) in a 2:1 mixture of ethanol and water (12 ml) $LiOH.H_2O$ (193.3 mg, 4.61 mmol) was added and heated at 40 ^{0}C for 19 hrs. Ethanol was evaporated under reduced pressure, the residual aqueous mixture was acidified to pH 1 and extracted with methylene chloride (2x40 ml). The organic extract was dried with $MgSO_4$

and evaporated under reduced pressure to give 2-(2-morpholin-4-yl-2-oxo-ethyl)-2-(3-phenyl-propyl)-malonic acid monoethyl ester as a thick, yellow oil (831 mg); ^{1}H NMR ($CDCl_3$) 7.4-7.1 (m, 6H), 4.25 (q, J=7.1Hz, 2H), 3.8-3.4 (m, 8H), 3.20 (d, J=16.4Hz, 1H), 2.9 (d, J=16.4Hz, 1H), 2.6 (m, 2H), 2.1-1.8 (m, 4H), 1.25 (t, J=7.1Hz, 3H). MS : 378 (MH^+).

2-(2-Morpholin-4-yl-2-oxo-ethyl)-5-phenyl-pentanoic acid ethyl ester (5)

A Solution of 2-(2-morpholin-4-yl-2-oxo-ethyl)-2-(3-phenyl-propyl)-malonic acid monoethyl ester (809 mg, 2.14 mmol) in toluene (25 ml) was heated under reflux for 23 hours. The colorless solution was concentrated under reduced pressure, the residue was taken up in diethyl ether (50 ml), washed with saturated $NaHCO_3$ and dried over $MgSO_4$. The solvent was evaporated under reduced pressure to give 2-(2-morpholin-4-yl-2-oxo-ethyl)-5-phenyl-pentanoic acid ethyl ester as yellow oil (617 mg); ^{1}H NMR ($CDCl_3$) 7.3-7.1 (m, 5H), 4.2 (m, 2H), 3.8-3.4 (m, 8H), 3.0 (m ,1H), 2.75 (dd, J=15.9, 9.4Hz, 1H), 2.65 (m, 2H), 2.35 (dd, J=15.9, 5.1Hz, 1H), 1.8-1.55 (m, 4H), 1.29 (t, J=7.1Hz, 3H). MS : 334 (MH^+).

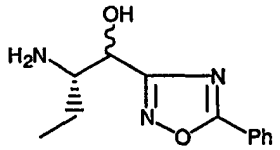
2-(2-Morpholin-4-yl-2-oxo-ethyl)-5-phenyl-pentanoic acid (6)

To a solution of 2-(2-morpholin-4-yl-2-oxo-ethyl)-5-phenyl-pentanoic acid ethyl ester (604 mg, 1.81 mmol) in a 2:1 mixture of MeOH-H_2O (12 ml) $LiOH.H_2O$ (228 mg, 5.43 mmol) was added and stirred overnight at room temperature. Ethanol was removed under reduced pressure, residue diluted with water (40 ml) and washed with ether. The aqueous layer was acidified to pH1 with 1N HCl and extracted with diethyl ether (3x 25 ml). The combined organic extracts were dried with $MgSO_4$ and concentrated under reduced pressure to give 2-(2-morpholin-4-yl-2-oxo-ethyl)-5-phenyl-pentanoic acid as a white solid (492 mg); ^{1}H NMR ($CDCl_3$) 8.0-7.5 (1H), 7.4-7.1 (m, 5H), 3.8-3.4 (m, 8H), 3.0 (m, 1H), 2.8 (dd, J=16.4, 9.6Hz, 1H), 2.65 (t, J=7.2Hz, 2H), 2.40 (dd, J=16.4, 4.3Hz, 1H),

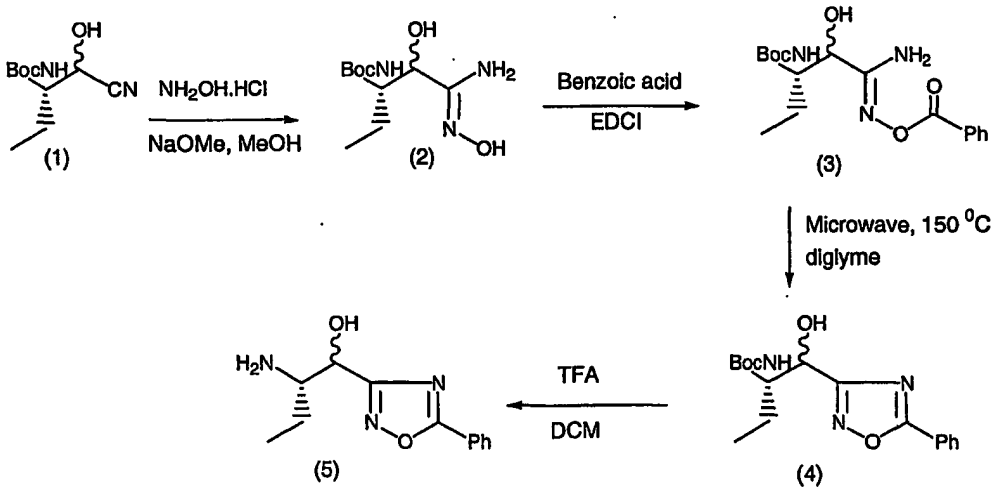
1.9-1.5 (m, 4H). MS : 306 (MH^+).

REFERENCE 26

2-Amino-1-(5-phenyl-[1,2,4]oxadiazol-3-yl)-butan-1-ol



Reference 26 was synthesized as described in the following reaction protocol:



{1-[Hydroxy-(N-hydroxycarbamimidoyl)-methyl]-propyl}-carbamic acid tert-butyl ester (2)

A solution of (2-cyano-1-ethyl-2-hydroxy-ethyl)-carbamic acid tert-butyl ester (9.53g, 44 mmol) in methanol (80 ml) was cooled to 0^0C and treated successively with hydroxylamine hydrochloride (3.05, 44 mmol) in methanol (80 ml) and 25% sodium

methoxide solution in methanol (10.2 ml). Stirred at 0°C for 5 minutes, cold bath removed and the reaction mixture stirred at room temperature for 5 hours. Methanol evaporated off under reduced pressure, crude partitioned between ethyl acetate and water. Organic layer separated, dried ($MgSO_4$) and evaporated under reduced pressure to give yellow oil. Purified by mplc, eluting with a mixture of ethyl acetate – heptane to give the title compound as white solid (3.5 g); MS: $M(H^+)$ 248.

{1-[Hydroxy-(N-benzoyloxycarbamimidoyl)-methyl]-propyl}-carbamic acid tert-butyl ester (3)

A solution of {1-[hydroxy-(*N*-hydroxycarbamimidoyl)-methyl]-propyl}-carbamic acid tert-butyl ester (2) (2.5g, 10 mmol) in dichloromethyl (125 ml) was treated with benzoic acid (1.36 g, 11 mmol), EDCI (2.14 g, 11mmol), HOBT (1.37 g, 10 mmol) and triethylamine (1.35 ml, 11 mmol) and stirred at room temperature overnight. Reaction mixture was washed with saturated sodium bicarbonate solution and then water and dried over Na_2SO_4. Solvent evaporated under reduced pressure, crude purified by mplc eluting with 1% triethylamine in 2:3 v/v ethyl acetate and heptane mixture to give yellow solid (850 mg); MS: MH^+ 352.

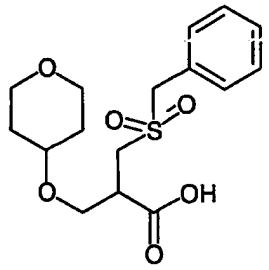
2-Amino-1-(5-phenyl-[1,2,4]oxadiazol-3-yl)-butan-1-ol (5)

A solution of (3) (1.5g, 4.3 mmol) in diglyme was heated at 150°C in a microwave (Smith Creator, S00219) for 40 minutes. Solvent evaporated under vacuum in Genevac Evaporator at 80°C for 3hours to give a brown solid. This was taken in dichloromethyl (40 ml) and treated with trifluoroacetic acid at room temperature for 2 hours. Solvent evaporated to dryness under reduced pressure, crude taken in water, washed with DCM, aqueous layer basified with 1M NaOH solution and extracted with dichloromethyl. Organic layer dried over Na_2SO_4 to give pale brown solid (300mg); ^{1}HNMR ($CDCl_3$) 8.14-8.10 (m, 2H), 7.59-7.47 (m, 3H), 4.83 & 4.65 (d, J= 5Hz, 1H), 3.18-3.05 (2m, 1H), 1.71-

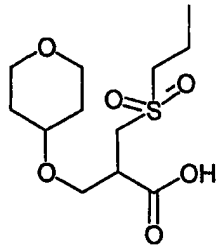
1.20(m, 2H), 1.05-0.97 (dt, J= 7.2Hz, 3H).

REFERENCE 27

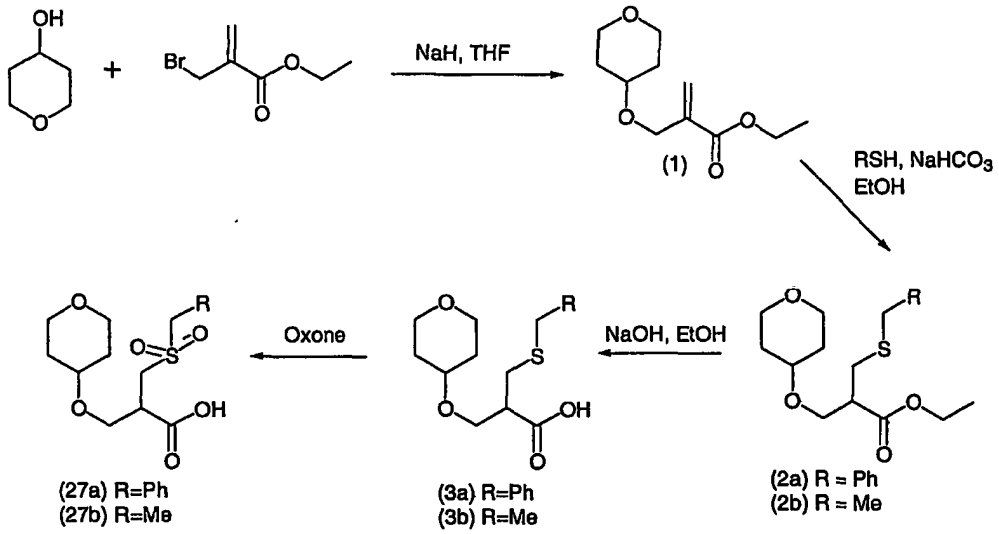
3-Benzylsulfonyl-2-(tetrahydro-pyran-4-yloxymethyl)-propionic acid (27a)



3-(Propane-1-sulfonyl)-2-(tetrahydro-pyran-4-yloxymethyl)-propionic acid (27b)



Compounds 27a and 27b were synthesized according to the following protocol:



2-(Tetrahydro-pyran-4-yloxymethyl)-acrylic acid ethyl ester (1)

NaH added to a solution of 4-hydroxy tetrahydropyran (5g, 49 mmol) in THF (40ml) stirred at room temperature for 30 minutes. A solution of ethyl 2-(bromomethyl) acrylate (9.6 g, 49 mmol) in THF (30 ml) was added and stirred at room temperature overnight. Reaction mixture cooled in ice, quenched with saturated NH_4Cl solution and extracted with ethyl acetate. Organic extracts dried, (Na_2SO_4) and purified by mplc eluting with 1:9 to 2:8 v/v ethyl acetate – heptane mixture to give the title compound as yellow oil (6.56g, 61%). MS: MH^+ 215; LCMS retention time 3.29 minutes.

3-Benzylsulfanyl-2-(tetrahydro-pyran-4-yloxymethyl)-propionic acid ethyl ester (2a)

A suspension of 2-(tetrahydro-pyran-4-yloxymethyl)-acrylic acid ethyl ester (2.2g, 10.2 mmol) in ethanol (100 ml) was treated with a solution of $NaHCO_3$ (0.86g, 10.2 mmol) in water ml (10ml) and benzyl mercapton (1.21 ml, 10.2 mmol) at room temperature overnight. Ethanol evaporated off under reduced pressure, crude partitioned between ethyl acetate and water, organic layer separated and purified by mplc eluting with 1:9 to 2:8 v/v

ethyl acetate –heptane mixture to give the title compound as pale yellow oil (1.27g). MS: 339 (MH^+); LCMS (Protocol B) retention time 4.3 minutes.

By using ethylmercapton 3-ethylsulfanyl-2-(tetrahydro-pyran-4-yloxymethyl)-propionic acid ethyl ester (2b) was similarly prepared; MS : 281 (MH^+); LCMS retention time 3.9 minutes.

3-Benzylsulfanyl-2-(tetrahydro-pyran-4-yloxymethyl)-propionic acid (3a)

A solution of 3-benzylsulfanyl-2-(tetrahydro-pyran-4-yloxymethyl)-propionic acid ethyl ester (1.27g) in ethanol (30ml) was treated with 2N NaOH (9.4 ml) overnight. Usual water work up gave the title compound as white solid; MS: 333 (M+Na), 311 (M+1); LCMS retention time 3.7 minutes.

3-Ethylsulfanyl-2-(tetrahydro-pyran-4-yloxymethyl)-propionic acid (3b) was similarly prepared by using 3-ethylsulfanyl-2-(tetrahydro-pyran-4-yloxymethyl)-propionic acid ethyl ester.

3-Benzylsulfonyl-2-(tetrahydro-pyran-4-yloxymethyl)-propionic acid (27a)

A solution of 3-Benzylsulfanyl-2-(tetrahydro-pyran-4-yloxymethyl)-propionic acid (1.16g, 3.7 mmol) in a mixture of MeOH (10 ml) and water (30 ml) was treated oxone (3.5 g, 5.6 mmol) overnight. Methanol evaporated off under reduced pressure, aqueous layer extracted with ethyl acetate, dried (Na_2SO_4) and evaporated under reduced pressure to give the title compound as white solid (1.36 g); MS: 365 (M+Na), 343 (MH^+); LCMS retention time 3.1 minutes.

3-ethylsulfonyl-2-(tetrahydro-pyran-4-yloxymethyl)-propionic acid (27b) was similarly prepared from 3-ethylsulfanyl-2-(tetrahydro-pyran-4-yloxymethyl)-propionic acid; MS: 303 (M+Na), 281 (MH^+); LCMS retention time 2.3 minutes.

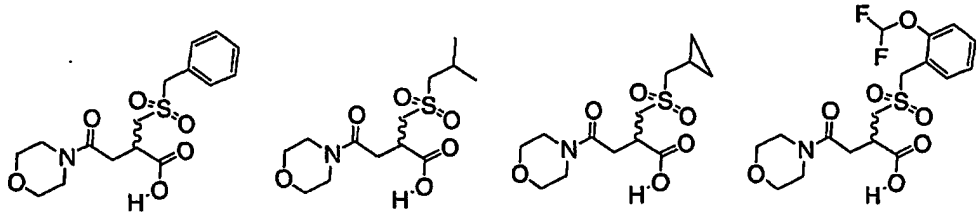
REFERENCE 28

4-Morpholin-4-yl-4-oxo-2-benzylsulfonylmethyl-butyric acid (28a);

2-(2-Methyl-propane-1-sulfonylmethyl)-4-morpholin-4-yl-4-oxo-butyric acid (28b);

2-Cyclopropylmethylsulfonylmethyl-4-morpholin-4-yl-4-oxo-butyric acid (28c); and

2-(2-Difluoromethoxy-benzylsulfonylmethyl)-4-morpholin-4-yl-4-oxo-butyric acid (28d)



(28a) (28b) (28c) (28d)

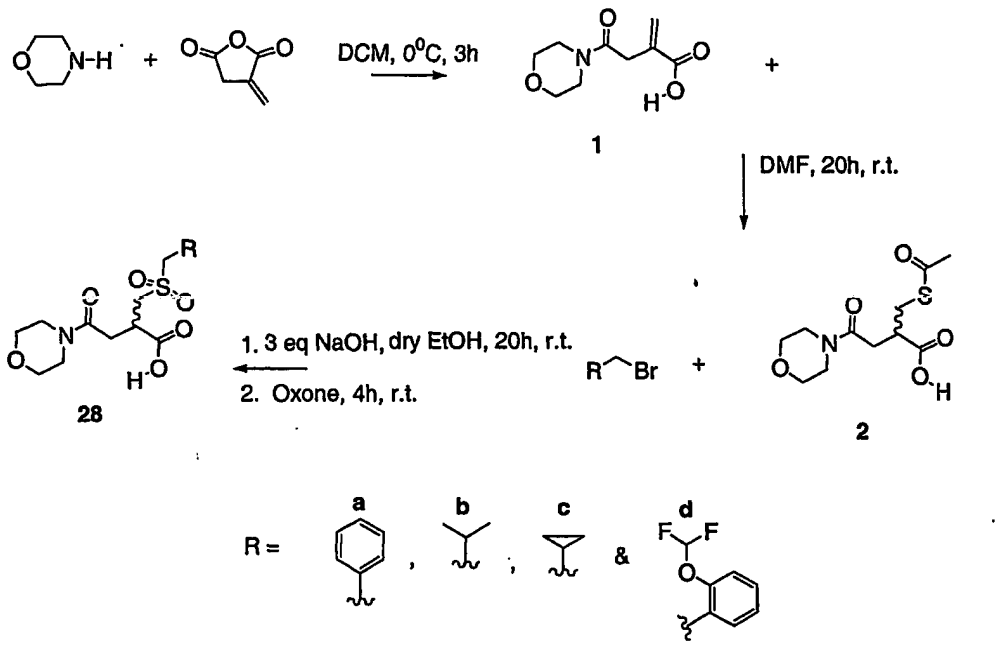
4-Morpholin-4-yl-4-oxo-2-benzylsulfonylmethyl-butyric acid (28a)

2-(2-Methyl-propane-1-sulfonylmethyl)-4-morpholin-4-yl-4-oxo-butyric acid (28b)

2-Cyclopropylmethylsulfonylmethyl-4-morpholin-4-yl-4-oxo-butyric acid (28c)

2-(2-Difluoromethoxy-benzylsulfonylmethyl)-4-morpholin-4-yl-4-oxo-butyric acid (28d)

Compounds 28a, b, c and d were synthesized according to the following protocol:



Synthesis of 2-(2-morpholin-4-yl-2-oxo-ethyl)-acrylic acid (1)

Morpholine (20mL, 228.6 mmol) was slowly added to a stirring solution of itaconic anhydride (25.1g, 228.6 mmol) suspended in dichloromethyl at 0°C. The reaction mixture was allowed to slowly warm to room temperature. Upon completion (LCMS), volatiles were removed by vacuum under reduced pressure. Crude yield: 44.96g, 99%. Product was used without further purification.

Synthesis of 2-Acetylsulfanylmethyl-4-morpholin-4-yl-4-oxo-butyric acid (2)

2-(2-morpholin-4-yl-2-oxo-ethyl)-acrylic acid (55.19g, 277.0 mmol) was dissolved in 120mL DMF and set to stir at room temperature. Potassium thioacetate (25g, 219.0 mmol) was added in one portion, and the reaction mixture was allowed to stir at ambient temperature for 20 hours. Upon completion (LCMS), DMF was removed by vacuum under reduced pressure. Crude Yield: 75g. Percent Purity (LCMS): 40%. The crude product was

used without further purification.

Synthesis of 4-morpholin-4-yl-4-oxo-2-benzylsulfonylmethyl-butyric acid (28a)

4-Morpholin-4-yl-4-oxo-2-benzylsulfonylmethyl-butyric acid (8.078g, 29.37 mmol) was dissolved in 100mL dry EtOH and set to stir at room temperature. NaOH pellets (3.52g, 88.0 mmol) were added in one portion, and the reaction mixture was allowed to stir for 10 minutes. Benzyl bromide (3.18mL, 26.7 mmol) was then added, and the reaction mixture was allowed to stir at ambient temperature for 20 hours. Upon completion (LCMS), the reaction mixture was diluted with water and the pH was lowered to ~pH2. The reaction mixture was then washed 3x with EtOAc. The organic phase was concentrated *in vacuo* and then diluted with 200mL aqueous MeOH. Oxone® (10.78g, 16.58 mmol) was added in one portion and the reaction was stirred at room temperature for 4 hours. Conversion of sulfide to sulfone was monitored via LCMS. Upon completion, reaction was quenched by the addition of sodium thiosulfate. Salts were filtered and the reaction mixture was washed 3X with ethyl acetate and dried over sodium sulfate. The organics were evaporated by vacuum under reduced pressure. The crude solid was crystallized from EtOAc. Yield 1.3g Percent Purity (NMR): 99%. *m/z* (LCMS) M^+ 356.01. δ_H 12.6 (1 H, br s), 7.4 (5 H, m), 4.5 (2 H, s), 3.5 (4 H, m), 3.5 (1 H, m), 3.4 (4 H, m), 3.2 (2 H, d), 2.75 (2 H, d).

Synthesis of 2-(2-Methyl-propane-1-sulfonylmethyl)-4-morpholin-4-yl-4-oxo-butyric acid (28b)

4-Morpholin-4-yl-4-oxo-2-benzylsulfonylmethyl-butyric acid (10.90g, 40.15 mmol) was dissolved in 100mL dry EtOH and set to stir at room temperature. NaOH pellets (4.81g, 120.45 mmol) were added in one portion, and the reaction mixture was allowed to stir for 10 minutes. 1-Bromo-2-methyl propane (5.0g, 36.49 mmol) was then added, and the reaction mixture was allowed to stir at ambient temperature for 20 hours. Upon completion (LCMS), the reaction mixture was diluted with water and the pH was lowered

to ~pH2. The reaction mixture was then washed 3x with EtOAc. The organic phase was concentrated *in vacuo* and then diluted with 200mL aqueous MeOH. Oxone (10.02g, 14.57 mmol) was added in one portion and the reaction was stirred at room temperature for 4 hours. Conversion of sulfide to sulfone was monitored via LCMS. Upon completion, reaction was quenched by the addition of sodium thiosulfate. Salts were filtered, and the reaction mixture was washed 3X with ethyl acetate and dried over sodium sulfate. The organics were evaporated by vacuum under reduced pressure. Product was purified via HPLC. Yield: 1.1g, 23.1%. *m/z* (LCMS) M^+ 322.01, $R_f = 2.03$. δ_H 12.6 (1 H, br s), 3.5 (4 H, m), 3.5 (1 H, m), 3.4 (4 H, m), 3.25 (2 H, d), 3.0 (2 H, m), 2.9 (2 H, d), 2.4 (1 H, m), 1.3 (6H, d d).

Synthesis of 2-Cyclopropylmethylsulfonylmethyl-4-morpholin-4-yl-4-oxo-butyric acid (28c)

4-Morpholin-4-yl-4-oxo-2-benzylsulfonylmethyl-butyric acid (11.16g, 40.74 mmol) was dissolved in 100mL dry EtOH and set to stir at room temperature. NaOH pellets (4.81g, 120.25 mmol) were added in one portion, and the reaction mixture was allowed to stir for 10 min. Bromomethylcyclopropane (5.0g, 37.04 mmol) was then added, and the reaction mixture was allowed to stir at ambient temperature for 20 hours. Upon completion (LCMS), the reaction mixture was diluted with water and the pH was lowered to ~pH2. The reaction mixture was then washed 3x with EtOAc. The organic phase was concentrated *in vacuo* and then diluted with 200mL aqueous MeOH. Oxone (15.6g, 24.0 mmol) was added in one portion and the reaction was stirred at room temperature for 4h. Conversion of sulfide to sulfone was monitored via LCMS. Upon completion, reaction was quenched by the addition of sodium thiosulfate. Salts were filtered, and the reaction mixture was washed 3X with ethyl acetate and dried over sodium sulfate. The organics were evaporated by vacuum under reduced pressure. Product was purified via HPLC. Yield: 1.2g, 15.1%. *m/z* (LCMS) M^+ 320.1, $R_f = 1.84$. δ_H 12.6 (1 H, br s), 3.5 (4 H, m), 3.5 (1 H, m), 3.4 (4 H, m), 3.25 (2 H, d), 3.0 (2 H, m), 2.9 (2 H, d), 2.4 (1 H, m), 1.1 (1 H, m), 0.62 (2 H, q), 0.38 (2 H, q).

Synthesis of 2-(2-Difluoromethoxy-benzylsulfonylmethyl)-4-morpholin-4-yl-4-oxo-butyric acid (28d)

4-Morpholin-4-yl-4-oxo-2-benzylsulfonylmethyl-butyric acid (1.27g, 4.64 mmol) was dissolved in 50mL dry EtOH and set to stir at room temperature. NaOH pellets (556mg, 13.92 mmol) were added in one portion, and the reaction mixture was allowed to stir for 10 min. 2-(Difluoromethoxy)-benzyl bromide (1.00g, 4.219 mmol) was then added, and the reaction mixture was allowed to stir at ambient temperature for 20h. Upon completion (LCMS), the reaction mixture was diluted with water and the pH was lowered to ~2. The reaction mixture was then washed 3x with EtOAc. The organic phase was concentrated *in vacuo* and then diluted with 100mL aqueous MeOH. Oxone (1.58g, 2.43 mmol) was added in one portion and the reaction was stirred at room temperature for 4h. Conversion of sulfide to sulfone was monitored via LCMS. Upon completion, reaction was quenched by the addition of sodium thiosulfate. Salts were filtered, and the reaction mixture was washed 3X with ethyl acetate and dried over sodium sulfate. The organics were evaporated by vacuum under reduced pressure. Product was purified via HPLC. Yield: 195mg, 19.0%. *m/z* (LCMS) M^+ 422.1. R_f = 2.42. δ_H 12.6 (1 H, br s), 7.6—7.2 (4 H, m), 7.19 (1 H, s) 4.5 (2 H, s), 3.5 (4 H, m), 3.5 (1 H, m), 3.4 (4 H, m), 3.2 (2 H, d), 2.75 (2 H, d).

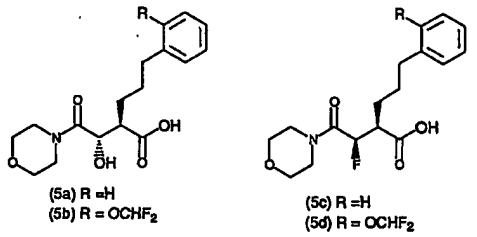
REFERENCE 29

(R)-2-((S)-1-Hydroxy-2-morpholin-4-yl-2-oxo-ethyl)-5-phenyl-pentanoic acid (5a)

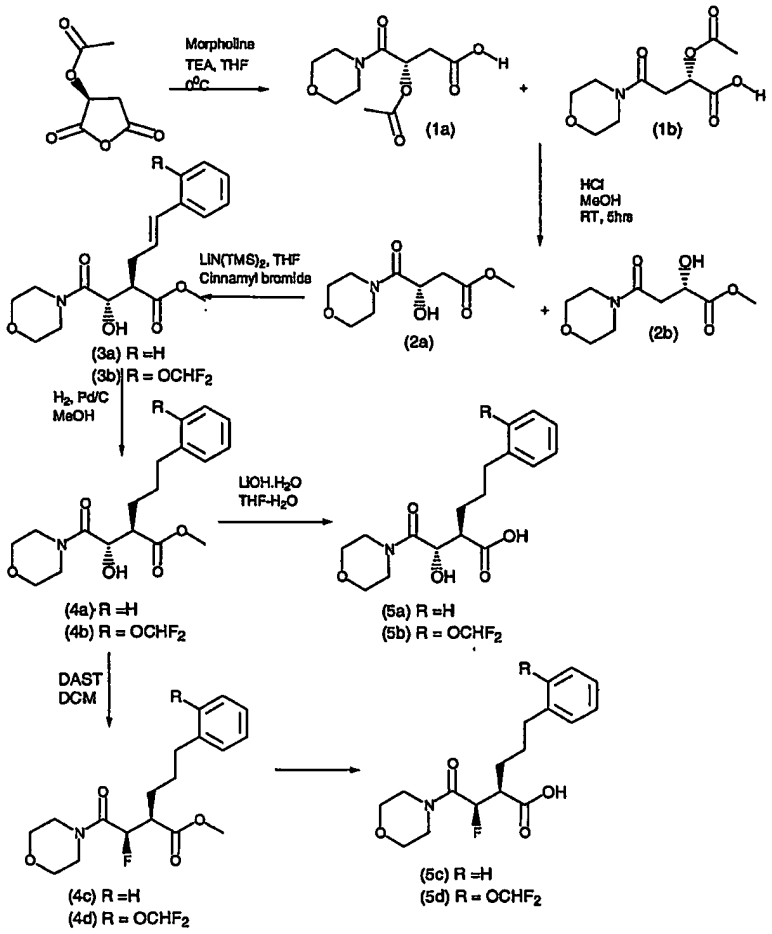
(R)-5-(2-Difluoromethoxy-phenyl)-2-((S)-1-hydroxy-2-morpholin-4-yl-2-oxo-ethyl)-pentanoic acid (5b)

(R)-2-((S)-1-Fluoro-2-morpholin-4-yl-2-oxo-ethyl)-5-phenyl-pentanoic acid (5c)

(R)-5-(2-Difluoromethoxy-phenyl)-2-((S)-1-fluoro-2-morpholin-4-yl-2-oxo-ethyl)-pentanoic acid (5d)



Compounds 5a, 5b, 5c and 5d were prepared according to the following reaction protocol:



5

(S)-3-Acetoxy-4-morpholin-4-yl-4-oxo-butyric acid (1a) &

(S)-2-Acetoxy-4-morpholin-4-yl-4-oxo-butyric acid (1b)

Morpholine (14.48 ml) and Triethylamine (23.14 ml, 166 mmol) were added to an

ice-cold solution of acetic acid (S)-2,5-dioxo-tetrahydro-furan-3-yl ester (25g, 158.12 mmol) in dry THF (600 ml) and the solution was stirred at room temperature over the week-end. Solvent was evaporated under reduced pressure, residue diluted with water, acidified to pH 2 with 1N HCl and extracted with ethyl acetate. Combined organic extracts were dried over $MgSO_4$ and evaporated under reduced pressure to give a mixture of (S)-3-acetoxy-4-morpholin-4-yl-4-oxo-butyric acid and 2-acetoxy-4-morpholin-4-yl-4-oxo-butyric acid (14g) as colorless oil. MS: 246 (MH^+).

(S)-3-Hydroxy-4-morpholin-4-yl-4-oxo-butyric acid methyl ester (2a)

To a mixture of (S)-3-acetoxy-4-morpholin-4-yl-4-oxo-butyric acid and 2-Acetoxy-4-morpholin-4-yl-4-oxo-butyric acid (11g, 44.8 mmol) in dry methanol (30 ml) HCl in dioxane (4M, 7.3 ml, 29.16 mmol) was added and stirred at room temperature for 5 hrs. The reaction mixture was neutralized with solid $NaHCO_3$, filtered through a mixture of Celite/Na_2SO_4 (1:1) and concentrated under reduced pressure to give a mixture of (S)-3-Hydroxy-4-morpholin-4-yl-4-oxo-butyric acid methyl ester and (S)-2-Hydroxy-4-morpholin-4-yl-4-oxo-butyric acid methyl ester. Column chromatography on silica eluting with a mixture of ethyl acetate and methylene chloride gave (S)-3-Hydroxy-4-morpholin-4-yl-4-oxo-butyric acid methyl ester, (6 g) as white solid; ^1H NMR ($CDCl_3$) δ 2.62 (d, J=8Hz, 2H), 3.78-3.44 (m, 11H), 3.76 (d, J=9Hz, 1H), 4.8-4.73 (m, 1H); MS: 218(MH^+).

(E)-(R)-2-((S)-1-Hydroxy-2-morpholin-4-yl-2-oxo-ethyl)-5-phenyl -pent-4-enoic acid methyl ester (3a)

Lithium hexamethyldisilazide (1M in THF, 14.5 ml, 14.5 mmol) was added to a solution of (S)-3-Hydroxy-4-morpholin-4-yl-4-oxo-butyric acid methyl ester (1.5g, 6.9 mmol) in dry THF (15 ml) at -78^0 C under N_2 and stirred for 30 min. Cinnamyl bromide (1.6g, 7.32 mmol) was then added, the reaction mixture stirred at $-78\ ^0$C for 2 hrs, warmed up to room temperature and stirred overnight at room temperature. The reaction was quenched with saturated ammonium chloride solution, adjusted the pH to 6 with 1N HCl and extracted with ethyl acetate. Combined ethyl acetate extracts were dried over $MgSO_4$

and concentrated under reduced pressure to give pale brown solid. Column chromatography on silica eluting with a mixture of ethyl acetate and methylene chloride gave the title compound as pale, yellow solid (1.15 g).

(E)-(R)-5-(2-Difluoromethoxy-phenyl)-2-((S)-1-hydroxy-2-morpholin-4-yl-2-oxo-ethyl)-pent-4-enoic acid methyl ester (3b)

Similarly prepared according to the procedure above but replacing cinnamyl bromide with1- ((E)-3-Bromo-propenyl)-2-difluoromethoxy-benzene.

(2R,3S)-2-Benzyl-3-hydroxy-4-morpholin-4-yl-4-oxo-butyric acid methyl ester (3c)

Similarly prepared according to the procedure above but replacing cinnamyl bromide with benzyl bromide.

(R)-2-((S)-1-Hydroxy-2-morpholin-4-yl-2-oxo-ethyl)-5-phenyl-pentanoic acid methyl ester (4a)

A solution of (E)-(R)-2-((S)-1-Hydroxy-2-morpholin-4-yl-2-oxo-ethyl)-5-phenyl-pent-4-enoic acid methyl ester (1.55g, 4.65 mmol) in methanol (15 ml) was hydrogenated at 50 psi over Pd/C for 4 hrs. The catalyst was removed by filtration through celite and the filtrate concentrated under reduced pressure to give (R)-2-((S)-1-Hydroxy-2-morpholin-4-yl-2-oxo-ethyl)-5-phenyl-pentanoic acid methyl ester as pale, brown solid (1.45 g); ^{1}H NMR ($CDCl_3$) δ 1.90-1.65 (m, 4H), 2.62-2.75 (m, 3H), 3.75-3.40 (m, 11H), 4.0 (d, J=15Hz, 1H), 4.47-4.4.39 (m, 1H), 7.38-7.15 (m, 5H); MS: 336(M^+).

(R)-5-(2-Difluoromethoxy-phenyl)-2-((S)-1-hydroxy-2-morpholin-4-yl-2-oxo-ethyl)-pentanoic acid methyl ester (4b)

Similarly prepared according to the procedure above but using (E)-(R)-5-(2-

Difluoromethoxy-phenyl)-2-((S)-1-hydroxy-2-morpholin-4-yl-2-oxo-ethyl)-pent-4-enoic acid methyl ester; ^{1}H NMR ($CDCl_3$) δ 1.93-1.58 (m, 4H), 2.78-2.58 (m, 3H), 3.80-3.42 (m, 11H), 4.03 (m, 1H), 4.44 (m, 1H), 6.53 (t, J=74Hz, 1H), 7.25-7.04 (m, 4H); MS: 402(MH^+).

(S)-2-((R)-1-Fluoro-2-morpholin-4-yl-2-oxo-ethyl)-5-phenyl -pentanoic acid methyl ester (4c)

(Diethylamino) sulfur trifluoride (2.0 ml, 15.2 mmol) was added to a ice cold solution of (R)-2-((S)-1-Hydroxy-2-morpholin-4-yl-2-oxo-ethyl)-5-phenyl-pentanoic acid methyl ester (4a) (0.85 g, 2.5 mmol) in dry methylene chloride (15 ml) and the reaction mixture was stirred overnight while warming to room temperature. The reaction was quenched with aqueous $NaHCO_3$ solution and extracted with methylene chloride. The organic extracts were dried over $Na2SO_4$ and concentrated under reduced pressure. Column chromatography on silica eluting with a mixture of ethyl acetate and methylene chloride gave the title compound as an off-white solid (230 mg). ^{1}H NMR ($CDCl_3$) δ 1.90-1.58 (m, 4H), 2.78-2.57 (m, 2H), 3.28-3.10 (m, 1H), 3.75 (s, 3H), 3.74-3.45 (m, 8H), 5.40-5.12 (m, 1H), 7.35-7.18 (m, 5H); MS: 338(MH^+).

(R)-2-((S)-1-Hydroxy-2-morpholin-4-yl-2-oxo-ethyl)-5-phenyl-pentanoic acid (5a)

A solution of (R)-2-((S)-1-hydroxy-2-morpholin-4-yl-2-oxo-ethyl)-5-phenyl-pentanoic acid methyl ester (230 mg, 0.69 mmol) and $LiOH.H_2O$ (57.5 mg, 1.37 mmol) in a mixture of THF and water (2:1, 6 ml) was stirred at room temperature for 2.5 hrs. The reaction was diluted with water and THF removed under reduced pressure. The pH of the aqueous solution was adjusted to pH5 with 1N HCl and extracted with ethyl acetate. The combined organic extracts were dried over $MgSO_4$ and evaporated under reduced pressure to give the title compound as white solid (180 mg); ^{1}H NMR ($CDCl_3$) δ 1.92-1.60 (m, 4H), 2.75-2.60 (m, 3H), 3.78-3.45 (m, 9H), 4.5 (d, J=8Hz, 1H), 7.35-7.18 (m, 5H); MS: 322(MH^+).

(R)-5-(2-Difluoromethoxy-phenyl)-2-((S)-1-hydroxy-2-morpholin

-4-yl-2-oxo-ethyl)-pentanoic acid (5b)

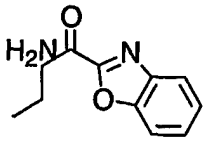
Similarly prepared according to the procedure above but using (R)-5-(2-difluoromethoxy-phenyl)-2-((S)-1-hydroxy-2-morpholin-4-yl-2-oxo-ethyl)-pentanoic acid methyl ester; ^{1}H NMR ($CDCl_3$) δ 1.90-1.65 (m, 4H), 2.77-2.68 (m, 3H), 3.70-3.53 (m, 9H), 4,51 (d, J=4.4Hz, 1H), 6.52 (t, J=74Hz, 1H), 7.28-7.14 (m, 4H); MS: 388(MH^+).

(2R,3S)-2-Benzyl-3-hydroxy-4-morpholin-4-yl-4-oxo-butyric acid (5e)

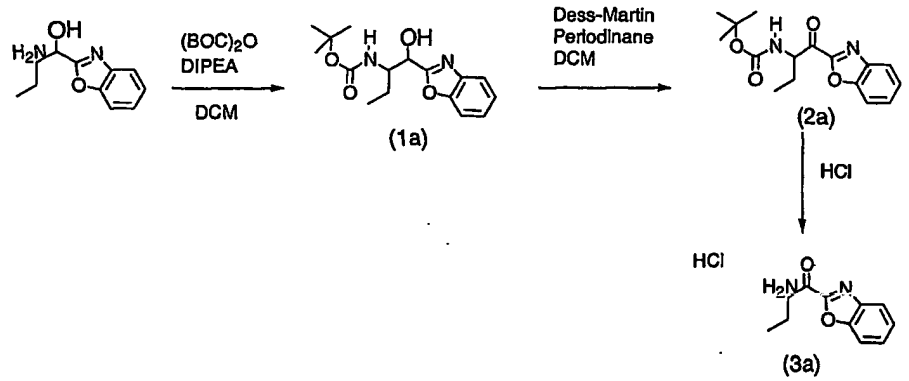
Similarly prepared according to the general procedure above but using (2R, 3S)-2-Benzyl-3-hydroxy-4-morpholin-4-yl-4-oxo-butyric acid methyl ester; ^{1}H NMR ($CDCl_3$) δ 2.90 (m, lH), 3.10 (m, 2H), 3.70-3.15 (m, 8H), 3.75 (m, 1H), 4.32 (d J=7.5Hz, 1H), 7.38-7.25 (m, 5H); MS: 294 (MH^+).

REFERENCE 30

2-Amino-1-benzooxazol-2-yl-butan-1-one



2-Amino-1-benzooxazol-2-yl-butan-1-one was prepared according to the following reaction protocol:



[1-(Benzooxazol-2-yl-hydroxy-methyl)-propyl]-carbamic acid tert-butyl ester (1a)

DIPEA (0.35 ml, 2 mmol) and di-tret-butyl dicarbonate (355 mg, 1.63 mmol) were added to a solution of 2-Amino-1-benzooxazol-2-yl-butan-1-ol (320 mg, 1.55 mmol) in dry methylene chloride (10 ml) and stirred at room temperature for 4 hrs. The reaction was quenched with saturated aqueous NH_4Cl and the pH was adjusted to neutral. Oraganic layer separated and the aqueous layer extracted with methylene chloride. The combined organic extracts were dried over $MgSO_4$ and concentrated under reduced pressure to give, 1-(Benzooxazol-2-yl-hydroxy-methyl)-propyl]-carbamic acid tert-butyl ester (500 mg).

[1-(Benzooxazole-2-carbonyl)-propyl]-carbamic acid tert-butyl ester (2a)

Dess-Martin Periodinane (15% in DCM, 3.1 mmol) was added to a solution of, 1-(Benzooxazol-2-yl-hydroxy-methyl)-propyl]-carbamic acid tert-butyl ester in dry methylene chloride (15 ml) and stirred at room temperature for 4 hrs. A solution of $Na_2S_2O_3$ in aqueous $NaHCO_3$ was added and stirred at room temperature. Organic layer was separated and the aqueous was extracted with methylene chloride. The combined organic extracts were dried over Na_2SO_4 and concentrated under reduced pressure to give a pale brown solid. Column chromatography on silica eluting with a mixture of methylene chloride and heptane gave the title compound as off white solid (380 mg).

2-Amino-1-benzooxazol-2-yl-butan-1-one hydrochloride (3a)

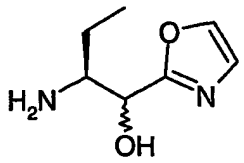
Hydrogen chloride in dioxane (1M, 1 ml) was added to a solution of, 1-(Benzooxazole-2-carbonyl)-propyl]-carbamic acid tert-butyl ester (2a) in dry methylene chloride (3 ml) and stirred at room temperature for 4 hrs. Concentration under reduced pressure gave the title compound as white solid (65 mg); ^{1}H NMR ($CDCl_3$) δ 0.99 (t, J=7.5Hz, 3H), 2.20-2.05 (m, 2H), 4.96 (m, 1H), 7.58 (t, J=7.4Hz, 1H), 7.69 (t, J=7.4Hz, 1H), 7.94 (d, J=8.2Hz, 1H), 8.04 (d, J=8.2Hz, 1H), 8.75 (m, 3H); MS: 207(MH^+).

(1-Amino-cyclopropyl)-oxazol-2-yl-methanone hydrochloride (3b)

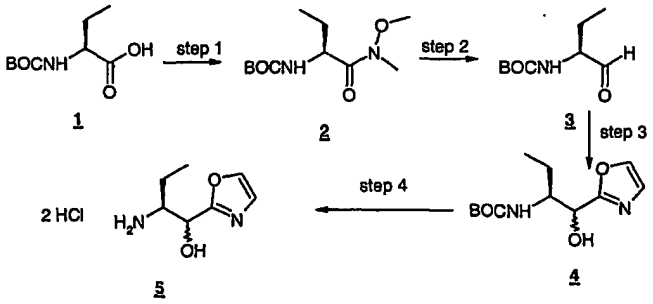
^{1}H NMR (DMSO) δ 1.79 (m, 2H), 1.22 (m, 2H), 7.58 (s, 1H), 8.49 (s, 1H), 9.22 (m, 3H); MS: 153(MH^+).

REFERENCE 31

2-Amino-1-oxazol-2-yl-butan-1-ol



2-Amino-1-oxazol-2-yl-butan-1-ol was prepared according to the following reaction scheme:



Step 1

To a stirring solution of of the BOC-L-α-aminobutyric acid (1, 17.75g, 87.3mmol) in dry methylene chloride (35ml) was added DIEA (33.45ml) followed by the N,O-dimethylhydroxylamine hydrochloride (9.37g, 96.03mmol) and PYBOP (50.0g, 96.03mmol). The reaction mixture was stirred overnight at room temperature. After the solvent was removed in vacuo, the oily residue was dissolved in ether and the precipitate which formed was filtered and the filtrate was concentrated to give 35.0g of a brown oil. The residue was dissolved in ethyl acetate and washed twice with 0.05N HCl, saturated sodium bicarbonate and brine. The organic layer was dried over magnesium sulfate and concentrated to give 14.0g of the product 2, which was used without further purification.

Step 2

Compound 2 (8.4g, 34.1mmol) was then dissolved in 30 ml of dry THF and cooled to -50° C under nitrogen, then LAH (1.0 M in THF, 37.5ml, 37.51mmol) was added drop wise over 30 minutes. The reaction was stirred for 1.5 hours at –50 ° C then allowed to warn to 0 ° C over 45 minutes. Then NaHSO4 (6.12g, 44.33mmol) was added slowly followed by cold water (2.0ml) and stirring was continued for 30 minutes. The reaction was filtered through celite, which was washed with methylene chloride. The volatiles were removed from the filtrate in vacuo. The solid residue was dissolved in ethyl acetate and washed with cold 0.05N HCl, water and brine. The organic layer was dried over magnesium sulfate, filtered and concentrated to give 6.5 grams of compound 3 as colorless oil.

Step 3

Triethylborane (1.0 M in THF, 149.5ml, 149.5mmol) was added to oxazole (10.33g, 149.5mmol) and stirred for 45 minutes at room temperature. The mixture was then cooled to –78 ° C and n-BuLi (2.5 M in hexane, 59.8ml, 149.5mmol) was added dropwise and allowed to stir for one hour under nitrogen. Compound 3 (8.0g, 42.7mmol) was dissolved in 25 ml of THF and added to the reaction mixture. The reaction was stirred for 5 hours at –78 ° C then it was allowed to warm to 0 ° C for one hour. The reaction was then cooled back to –78 ° C and quenched with 7% acetic acid in ethanol (700ml) which

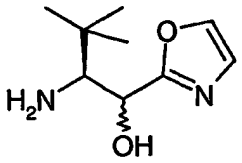
was allowed to stir overnight at room temperature. The mixture was concentrated in vacuo and the residue was dissolved in ether and filtered. The filtrate was concentrated in vacuo and the residue was dissolved in ethyl acetate washed twice with 0.005 N HCl, twice with sat'd sodium bicarbonate and brine. The organic layer was dried over magnesium sulfate, filtered and concentrated in vacuo. The residue was purified on silica using 10-40% ethyl acetate/heptane to give 3.85 grams of pure product 4.

Step 4

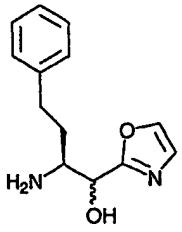
To a solution of compound 4 (1.1g, 4.29mmol) in dry methylene chloride (10.0ml), stirring under nitrogen at room temperature, was added 4M HCl (in dioxane, 10.73ml) dropwise followed by 5 ml of methanol. The reaction was stirred overnight then concentrated in vacuo to give 1.2 grams of compound 5 as a brown solid.

The following reference compounds were prepared according to the protocol described in Reference 31:

2-Amino-3,3-dimethyl-1-oxazol-2-yl-butan-1-ol



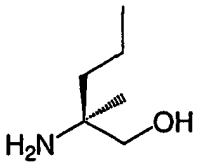
2-Amino-1-oxazol-2-yl-4-phenyl-butan-1-ol



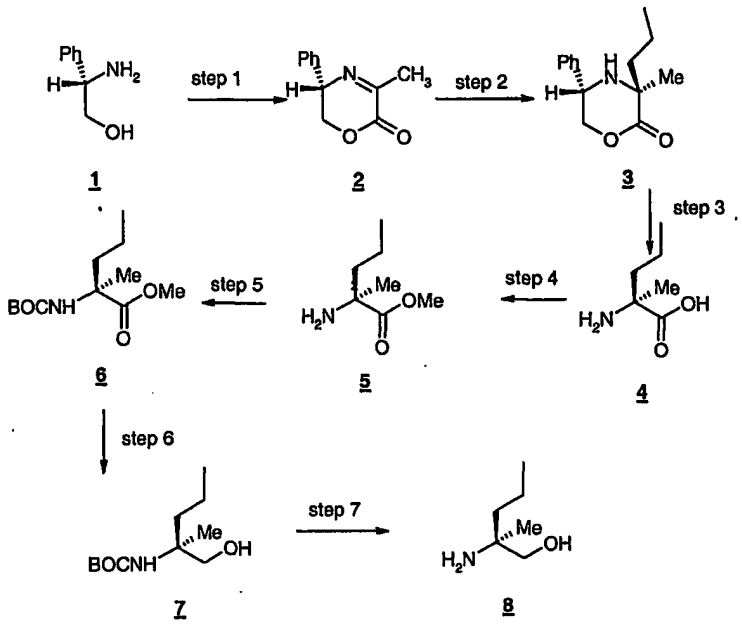
LCMS retention time 1.10 minutes; M+1 (233.1)

REFERENCE 32

2-Amino-2-methyl-pentan-1-ol



2-Amino-2-methyl-pentan-1-ol was prepared according to the following reaction scheme:



Step 1

S-(+)-Phenylglycinol (1, 25g,182mmol) was dissolved in trifluoroethanol (250ml) and ethyl pyruvate (23.3g, 200mmol) was added (exothermic) followed by molecular seives (4 angstroms) and the reaction was refluxed overnight. The reaction was filtered and concentrated to an oil. The oil was purified on a 500 g silica gel column and eluted with 3:1 heptane/ethyl acetate to give 19.94 grams of compound 2.

Step 2

Compound 2 (15.0g, 79mmol) was dissolved in THF (400ml) and cooled to –78 °

C, the boron trifluoride etherate (22.4g, 158mmol) was added over a 15 minute period. The reaction was allowed to stir at –78 degree C for 2 hours and propyl magnesium chloride (2.0 M in ether, 79ml, 158mmol) was added over a one hour period and allowed to stir for 4 hours at –78 ° C. The reaction was allowed to warm to room temperature and stir overnight. The mixture was carefully quenched with sat'd NaHSO4 until pH of 8 was obtained. The reaction was extracted with ethyl acetate (2x200ml), then washed with water, brine, dried over sodium sulfate and concentrated to dryness. The residue was purified on silica eluting with 4:1 heptane/ethyl acetate to give 12.2 grams of compound **3**.

Steps 3 and 4

Compound **3** (9.0g, 39mmol) was dissolved in ethanol (100ml) and water (20ml) followed by the addition of 9 grams of Pd(OH)2 and TFA (4ml). The mixture was hydrogenated at 50 psi for 48 hours, then the reaction was filtered through celite which was concentrated to give 9 grams of crude material **4** which was used without further purification. Compound **4** was dissolved in dry methanol (300ml) and HCl gas was bubbled through for 15 minutes. The reaction was stirred at room temperature for three days and was concentrated. The crude product was purified on silica eluting With 1:1 heptane/ethyl acetate to give 3.9 grams of compound **5**.

Step 5

A mixture of compound **5** (3.9g, 27mmol), (BOC)2O (5.88g, 27mmol), and TEA (7.56ml, 54mmol) in 100 ml of dioxane and 100ml of water were stirred overnight at room temperature. The reaction mixture was concentrated and dissolved in ethyl acetate and washed with brine. The organic layer was dried over magnesium sulfate, filtered and concentrated in vacuo. The crude product was purified on silica eluting with 30 ethyl acetate/heptane to give 6.68 gram of pure product **6**.

Step 6

A solution of compound **6** (6.68g, 27mmol) in 200ml of THF was cooled to 0 ° C and LAH (1.0M in THF, 32.4ml, 32.4mmol) was added dropwise and the reaction was stirred for 30 minutes then allowed to come to room temperature. The reaction was stirred

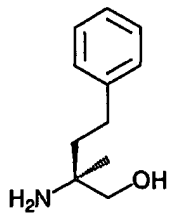
for another 30 minutes and the reaction was quenched with a solution of NaHS04, the THF was removed in vacuo and the residue was extracted with ethyl acetate which was washed with brine and concentrated. The product was purified on silica eluting with n-heptane to 5% methanol/ethyl acetate to give 2.8767 g of compound 7.

Step 7

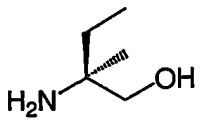
Compound 7 (0.5g) was dissolved in 5 ml of 4N HCL in dioxane and stirred for 1 hour at room temperature. The reaction was concentrated and dried under high vacuum to give 0.3859g of compound 8, which was used without further purification.

The following reference compounds were prepared according to the protocol described in Reference 32:

2-Amino-2-methyl-4-phenyl-butan-1-ol

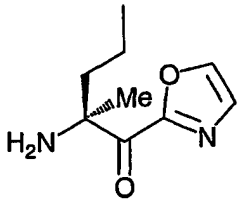


2-Amino-2-methyl-butan-1-ol

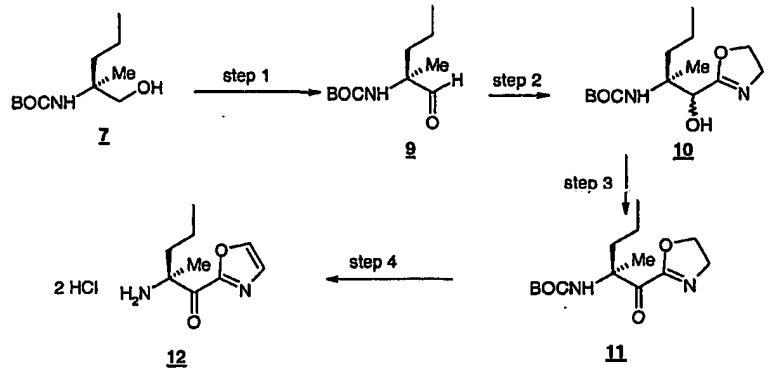


REFERENCE 33

2-Amino-2-methyl-1-oxazol-2-yl-pentan-1-one



2-Amino-2-methyl-1-oxazol-2-yl-pentan-1-one was prepared according to the following reaction scheme:



Step 1

A solution of oxalyl chloride (2.0M in CH2Cl2, 1.5ml, 3mmol) in 5 ml of methylene chloride was cooled to –78 ° C, then DMSO (0.44ml) was added drop wise to the mixture and allowed to stir for 5 minutes. A solution of compound 7 (Scheme 2, 0.4346g, 2.0mmol) in 10 ml of methylene chloride was added drop wise. The reaction was stirred at –78 degree C for 15 minutes and TEA (1.12ml, 8mmol) was added dropwise and the reaction was stirred for 2 hours at room temperature. The reaction was quenched with water and the product was extracted with ethyl acetate, then organic layer was washed with brine and the solvent was removed in vacuo. The crude product was purified on silica eluting with heptane to 10% ethyl acetate/heptane to give 0.3131 g of pure compound **9**.

Step 2

Triethylborane (1.0 M in THF, 4.84ml, 4.84mmol) was added to oxazole (0.3355g, 4.84mmol) in 4 ml of THF and stirred for 30 minutes at room temperature. The mixture was then cooled to –78 ° C and n-BuLi (1.6 M in hexane, 3.025ml, 4.84mmol) was added dropwise and allowed to stir for one hour under nitrogen. Compound **9** (0.2615g, 1.21mmol) was dissolved in 5 ml of THF and added to the reaction mixture. The reaction was stirred for 5 hours at –78 ° C, then quenched with 5% acetic acid in ethanol (20ml) which was allowed to stir overnight at room temperature and concentrated in vacuo. Ether was added and the solid was filtered and the filtrate was concentrated and the crude product

was purified on silica using 0-20% ethyl acetate/heptane to give 0.2528 grams of pure product **10**.

Step 3

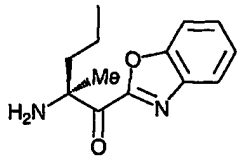
Dess-Martin periodinane (15% in CH2Cl2, 4.95g, 1.8mmol) was added to a stirring added to a stirring solution of compound **10** (0.2528g, 0.89mmol) in 5 ml of methylene chloride. The reaction was stirred at room temperature for 3 hours, then the reaction was quenched with a solution of sodium thiosulfate in sat'd sodium bicarbonate. The product was extracted with ethyl acetate and the organic layer was washed with brine, dried over magnesium sulfate and concentrated in vacuo. The residue was purified on silica eluting with 1:1 ethyl acetate/heptane to 5% methanol/ethyl acetate to give 0.2307 g of pure compound **11**.

Step 4

Compound **11** (0.2123g, 0.75mmol) was dissolved in 5 ml of 4N HCL in dioxane and stirred for 1 hour at room temperature. The reaction was concentrated and dried under high vacuum to give 0.1713g of compound **8**, which was used without further purification.

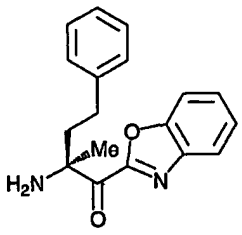
The following reference compounds were prepared according to the protocol described in Reference 33:

2-Amino-1-benzooxazol-2-yl-2-methyl-pentan-1-one



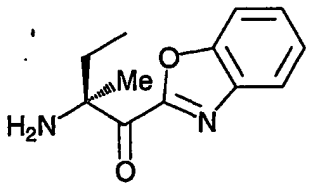
LCMS retention time 2.45 minutes; M+1 (233.1).

2-Amino-1-benzooxazol-2-yl-2-methyl-4-phenyl-butan-1-one



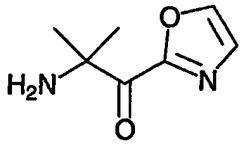
LCMS retention time 2.79 minutes; M+1 (295.1)

2-Amino-1-benzooxazol-2-yl-2-methyl-butan-1-one



LCMS retention time 2.29 minutes; M+1 (219.1)

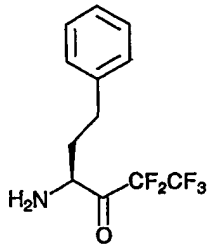
2-Amino-2-methyl-1-oxazol-2-yl-propan-1-one



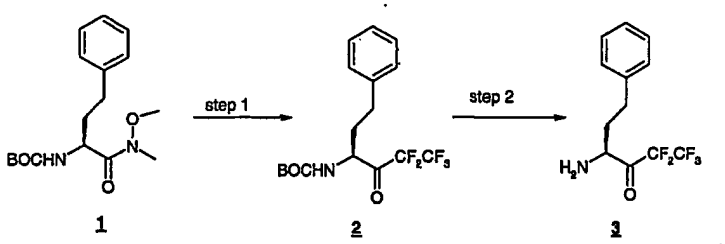
LCMS retention time 1.63 minutes; M+1 (155.1)

REFERENCE 34

2-Amino-4-phenyl-butyramide



2-Amino-4-phenyl-butyramide was prepared according to the following reaction scheme:



Step 1

Compound 1 (5g, 15.5mmol) was dissolved in dry ether (150ml) and cooled to –20° C, then perfluoroethyl iodide (25g, 100mmol) was bubbled into the mixture. The solution was then cooled to –50° C and methyl lithium/lithium bromide complex was added over a 30 minute period. The reaction was stirred for 1.5 hours at this temperature and was then quenched with acetone. After stirring for 15 minutes the reaction was diluted with ether (100ml) and poured onto 100ml of water contain KHSO4. The organic layer was separated and washed with water, brine, dried over sodium sulfate and concentrated to dryness. The material was purified on silica eluting with 1:1 ethyl acetate/heptane to give 1.7 grams of compound 2.

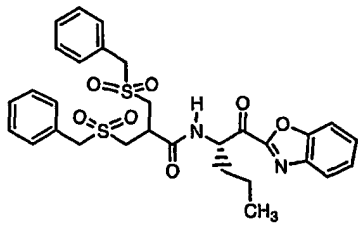
Step 2

Compound 2 (0.35g) was dissolved in 4 ml of 4N HCL in dioxane and stirred for 1 hour at room temperature. The reaction was concentrated and dried under high vacuum to give 0.2807g of compound 3 which was used without further purification; LCMS retention time 4.19 minutes; M+1 (282.1).

EXAMPLE 1

N-[(S)-1-(1-Benzooxazol-2-yl-methanoyl)-butyl]-3-benzylsulfonyl-2-benzylsulfonylmethyl-propionamide

(Compound 1)



A mixture comprised of 3-benzylsulfanyl-2-benzylsulfanylmethyl-propionic acid (0.239g, 0.719 mmol), prepared as in Reference 1, in methylene chloride (6 mL), HOBt hydrate (0.11g, 0.719 mmol), EDC (0.18g, 0.939 mmol), hydroxy amine (0.19 g, 0.86 mmol) and 4-methylmorpholine (0.075 mL) was stirred at room temperature for 1 hour and then poured into cold 1N aqueous hydrochloric. The product was extracted with ethyl acetate and the extracts were washed with saturated aqueous sodium chloride and then dried over magnesium sulfate. The solvent was removed by rotary evaporation at reduced pressure and the residue was chromatographed on silica gel eluting with ethyl acetate/hexane to give *N*-[(S)-1-(1-Benzooxazol-2-yl-1-hydroxy-methyl)-butyl]-3-benzylsulfanyl-2-benzylsulfanylmethyl-propionamide (0.217 g).

A solution of *N*-[(S)-1-(1-Benzooxazol-2-yl-1-hydroxy-methyl)-butyl]-3-benzylsulfanyl-2-benzylsulfanylmethyl-propionamide (0.317 g, 0.594 mmol) in methanol (30 mL) was treated with a solution of Oxone® (0.913 g, 1.48 mmol) in water (20 mL) and then stirred at room temperature for 7 hours. The methanol was removed by evaporation at reduced pressure and the resulting suspension was diluted with water and the product extracted with ethyl acetate. The extracts were washed with saturated aqueous sodium chloride and then dried over magnesium sulfate. The solvent was removed by rotary evaporation at reduced pressure and the residue was chromatographed on silica gel eluting with ethyl acetate/hexane to give *N*-[(S)-1-(1-Benzooxazol-2-yl-1-hydroxy-methyl)-butyl]-3-benzylsulfonyl-2-benzylsulfonylmethyl-propionamide (0.143 g, 41% yield).

A solution of *N*-[(S)-1-(1-Benzooxazol-2-yl-1-hydroxy-methyl)-butyl]-3-benzylsulfonyl-2-benzylsulfonylmethyl-propionamide (0.140 g, 0.234 mmol) in methylene chloride (5 mL) was treated with 1,1,1,1-triacetoxy-1,1-dihydro-1,2-benziodoxol-3(1H)-one (Dess-Martin periodinane) (0.127 g, 0.30 mmoL) and the resulting solution was stirred at room temperature for 30 minutes. Aqueous sodium thiosulfate and sodium bicarbonate

(15 mL, 0.25 M) were added and the reaction mixture was stirred for 20 minutes. The product was extracted with ethyl acetate. The extracts were washed with saturated aqueous sodium chloride and then dried over magnesium sulfate. The solvent was removed by rotary evaporation at reduced pressure and the residue was crystallized from t-butylmethyl ether to give *N*-[(S)-1-(1-benzooxazol-2-yl-methanoyl)-butyl]-3-benzylsulfonyl-2-benzyl-sulfonylmethyl-propionamide (0.103 g, 74%); NMR (DMSO): 9.15 (d, J=6Hz, 1H); 8.01 (d, J=7Hz, 1H); 7.89 (d, J=8Hz, 1H); 7.65 (t, J=7Hz, 1H); 7.54 (t, J=8Hz, 1H); 7.37 (m, 10H); 5.36 (m, 1H); 4.5 (m, 4H); 3.68 (m, 1H); 3.45-3.25 (m, 4H); 1.95 (m, 1H); 1.73 (m, 1H); 1.47 (m, 2H); 0.91 (t, J=7Hz, 3H); MS: M(H+) 597.0 (596.17);

The following compounds were prepared by the method of Example 1 by substituting the required carboxylic acid in place of 3-benzylsulfanyl-2-benzylsulfanylmethyl-propionic acid:

N-[(S)-1-(1-Benzooxazol-2-yl-methanoyl)-butyl]-3-(2-trifluoromethyl-benzylsulfonyl)-2-(2-trifluoromethyl-benzylsulfonylmethyl)-propionamide (Compound 2); ^{1}H-NMR ($CDCl_3$) δ: 7.93 (m, 1H); 7.69 (m, 4H); 7.4-7.6 (m, 6H); 7.20 (m, 2H); 5.58 (m, 1H); 4.54 (m, 4H); 3.69 (m, 1H); 3.30-3.55 (m, 4H); 1.55-1.90 (m, 1H); 1.45 (m, 1H); 1.32 (m, 2H); 0.90 (m, 3H); MS: M(+) 733.0; M(-) 731.6;

N-[(S)-1-(1-Benzooxazol-2-yl-methanoyl)-pentyl]-4-(2-methoxy-benzenesulfonyl)-2-[2-(2-methoxy-benzenesulfonyl)-ethyl]-butyramide (Compound 3); ^{1}H-NMR (DMSO) δ: 8.65 (d, 1H); 7.99 (d, J=7Hz, 1H); 7.89 (d, J=8Hz, 1H); 7.8-7.5 (m, 6H); 7.3-7.1 (m, 4H); 5.25 (m, 1H); 3.90 (m, 9H); 3.3 (m, 6H); 1.6 (m, 4H); 1.3 (m, 2H); 0.85 (m, 3H); MS: (M+) 670.2, 670.19;

4-Benzenesulfonyl-2-(2-benzenesulfonyl-ethyl)-*N*-[(S)-1-(1-benzooxazol-2-yl-methanoyl)-butyl]-butyramide (Compound 4); ^{1}H-NMR (DMSO) δ: 8.61 (d, J=6Hz, 1H); 7.99 (d, J=8Hz, 1H); 7.91 (d, J=8Hz, 1H); 7.82 (m, 4H); 7.74 (m, 2H); 7.64 (m, 5H); 7.55 (t, J=8Hz, 1H); 5.21 (m, 1H); 3.3-3.0 (m, 5H); 1.8 (m, 1H); 1.6 (m, 5H); 1.3 (m, 2H); 0.86 (t, J=7Hz, 3H); MS: (M+) 597.2, 596.17;

(R)-*N*-[(S)-1-(1-Benzooxazol-2-yl-methanoyl)-butyl]-2-cyclohexylmethyl-3-benzylsulfonyl-propionamide (Compound 5) ; ^{1}H NMR (DMSO): 8.96 (d, J=6Hz, 1H), 8.73 (d, J=6Hz, 1H), 7.99 (d, J=8H, 1H), 7.87 (m, 1H), 7.64 (m, 1H), 7.54 (m, 1H), 7.37

(m, 5H), 5.29 (m, 1H), 4.44 (s, 2H), 4.36 (s, 2H), 3.3-2.8 (m, 2H), 0.6-2.0 (m, 20H); MS: MH^+ 525.4 (524.23); and

N-[(S)-1-(1-Benzothiazol-2-yl-methanoyl)-propyl]-4-morpholin-4-yl-4-oxo-2-benzylsulfonylmethyl-butyramide (Compound 6); ^{1}H NMR: (DMSO), 8.79 (d, J=6.2Hz), 8.72 (d, J=6.2Hz), 1H], 8.30-8.22 (m, 2H), 7.71-7.61 (m, 2H), 7.43-7.33 (m, 5H), 5.46-5.33 (m, 1H), 4.53-4.38 (m, 2H), 3.57-3.30 (m, 10H), 3.13-3.02 (m, 1H), 2.66-2.54 (m, 2H), 2.04-1.90 (m, 1H), 1.83-1.68 (m, 1H), 0.97 (t, J=7.2Hz, 3H); MS: (M^++1) 558.

The method of Example 1 can also be modified by omitting the Oxone® oxidation step to prepare the following compounds:

N-[(S)-1-(1-Benzooxazol-2-yl-methanoyl)-butyl]-3-cyclohexyl-2-cyclohexylmethyl-propionamide (Compound 7); ^{1}H NMR (DMSO): 8.50 (d, J=6Hz, 1H); 8.00 (d, J=8Hz, 1H); 7.89 (d, J=8Hz, 1H); 7.62 (t, J=7Hz, 1H); 7.53 (t, J=7Hz, 1H); 5.2(m, 1H); 2.0-0.8 (m, 35H); MS: M(H+) 453.2 (452.3);

N-[(S)-1-(1-Benzooxazol-2-yl-methanoyl)-butyl]-3-isobutylsulfanyl-2-isobutylsulfanylmethyl-propionamide (Compound 8); ^{1}H NMR (DMSO): 8.73 (d, J=5Hz, 1H); 7.76 (d, J=7Hz, 1H); 7.87 (d, J=8Hz, 1H); 7.62 (dt, J=7,1Hz, 1H); 7.52 (dt, J=8,1Hz, 1H); 5.26 (m, 1H); 2.7 (m, 1H); 2.55 (m, 4H); 2.34 (d, J=7Hz, 2H); 2.29 (d, J=7Hz, 2H); 1.9 (m, 1H); 1.66 (m, 3H); 1.45 (m, 2H); 0.91 (t, J=6Hz, 3H), 0.90 (d, J=6Hz, 6H), 0.88 (d, J=3Hz, 3H), 0.84 (d, J=3Hz, 3H); MS: M(H+) 465.0 (464.22);

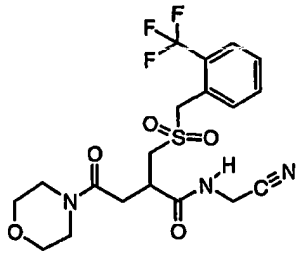
N-[(S)-1-(1-Benzooxazol-2-yl-methanoyl)-butyl]-3-benzylsulfanyl-2-benzylsulfanylmethyl-propionamide (Compound 9); ^{1}H NMR (DMSO): 8.80 (d, J=7Hz, 1H); 7.98 (d, J=8Hz, 1H); 7.88 (d, J=8Hz, 1H); 7.63 (t, J=7Hz, 1H); 7.53 (t, J=7Hz, 1H); 7.3-7.2 (m, 10H); 5.32 (m, 1H); 3.71 (s, 2H); 3.65 (d, J=3Hz, 2H); 2.87 (m, 1H); 2.45-2.3 (m, 4H); 2.0-1.4 (m, 4H); 0.92 (t, J=7Hz, 3H); MS: M(H+) 533.0 (532.19); and

N-[(S)-1-(1-Benzooxazol-2-yl-methanoyl)-butyl]-4-phenylsulfanyl-2-(2-phenylsulfanyl-ethyl)-butyramide (Compound 10); ^{1}H NMR (DMSO): 8.73 (d, J=6Hz, 1H); 7.99 (d, J=8Hz, 1H); 7.88 (d, J=8Hz, 1H); 7.65 (t, J=8Hz, 1H); 7.53 (t, J=8Hz, 1H); 7.35-7.1 (m, 10H); 5.3 (m, 1H); 2.85 (m, 4H); 2.65 (m, 1H); 2.0-1.3 (m, 8H); 0.91 (t, J=7Hz, 3H); MS: M(H+) 533.0 (532.19).

EXAMPLE 2

N-Cyanomethyl-4-morpholin-4-yl-4-oxo-2-(2-trifluoromethyl-benzyl-sulfonylmethyl)-butyramide

(Compound 11)



A mixture comprised of 4-morpholin-4-yl-4-oxo-2-(2-trifluoromethyl-benzylsulfonylmethyl)-butyric acid (200mg, 0.47mmol), prepared as in reference 5, EDC (200mg, 1.05mmol), HOBt (200mg, 1.3mmol), and aminoacetonitrile hydrochloride (150mg, 1.6mmol) was treated with dichloromethyl (4mL) and 4-methylmorpholine (0.5mL). The mixture was stirred at ambient temperature for 2 hours. After dilution with ethyl acetate (150mL), the solution was washed with water (30mL), saturated aqueous $NaHCO_3$ solution and brine, dried with magnesium sulfate and evaporated under vacuum. The product was crystallized from ethyl acetate/hexane to yield *N*-cyanomethyl-4-morpholin-4-yl-4-oxo-2-(2-trifluoromethyl-benzyl-sulfonylmethyl)-butyramide (156mg) as a yellowish solid; ^{1}H NMR: (DMSO) 8.87 (t, J=5.5Hz, 1H), 7.81-7.57 (m, 4H), 4.74 (d, J=14.5Hz, 1H), 4.67 (d, J=14.5Hz, 1H), 4.13 (d, J=5.5Hz, 2H), 3.63-3.26 (m, 11H), 2.75 (dd, J=6.4Hz, J=16.8Hz, 1H), 2.65 (dd, J=6.2Hz, J=16.8Hz, 1H); MS: (M^++1) 462;

The following compounds of Formula I were provided by proceeding as in Example 2:

N^4-(4-Carbamoyl-phenyl)-N^1-cyanomethyl-2-benzyl-sulfonylmethyl-succinamide (Compound 19); ^{1}H NMR: (DMSO) 10.24 (s, 1H), 8.93 (t, J=5.5Hz, 1H), 7.83 (s, 1H), 7.81 (d, J=8.4Hz, 2H), 7.60 (d, J=8.4Hz, 2H), 7.44-7.35 (m, 5H), 7.23 (s, 1H), 4.53 (d,

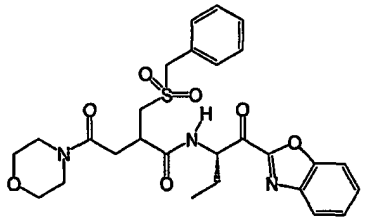
J=13.6Hz, 1H), 4.48 (d, J=13.6Hz, 1H), 4.14 (m, 2H), 3.50-3.30 (m, 2H), 3.20 (dd, J=4.7Hz, J=13.1Hz, 1H), 2.73 (d, J=6.7Hz, 2H); MS: (M^++1) 443; and

N-Cyanomethyl-2-[2-(1,1-difluoro-methoxy)-benzylsulfonylmethyl]-4-morpholin-4-yl-4-oxo-butyramide (Compound 25); ^{1}H NMR: (DMSO) 8.85 (t, J=5.5Hz, 1H), 7.52-7.43 (m, 2H), 7.31-7.22 (m, 2H), 7.13 (t, $J_{H,F}$=74Hz, 1H), 4.53 (s, 2H), 4.11 (d, J=5.5Hz, 2H), 3.58-3.20 (m, 11H), 2.72 (dd, J=6.7Hz, J=16.8Hz, 1H), 2.63 (dd, J=5.9Hz, J=16.8Hz, 1H); MS: (M^++1) 460;

EXAMPLE 3

N-[(S)-1-(1-Benzooxazol-2-yl-methanoyl)-propyl]-4-morpholin-4-yl-4-oxo-2-benzylsulfonylmethyl-butyramide

(Compound 29)



A mixture comprised of 4-Morpholin-4-yl-4-oxo-2-(benzyl-sulfonylmethyl)-butyric acid (300mg, 0.84mmol), EDC (250mg, 1.3mmol), HOBt (250mg, 1.6mmol) and (2S)-2-amino-1-benzooxazol-2-yl-butan-1-ol (250mg, 1.2mmol) was treated with dichloromethyl (4mL) followed by 4-methylmorpholine (0.5mL). The mixture was stirred at ambient temperature for 2 hours. After dilution with ethyl acetate (150mL), the solution was washed with 1N aqueous HCl, water, saturated aqueous $NaHCO_3$ solution and brine, dried with magnesium sulfate and evaporated under vacuum. The crude product was dissolved in dry dichloromethyl (10mL) and 1,1,1,1-triacetoxy-1,1-dihydro-1,2-benziodoxol-3(1H)-one (Dess-Martin periodinane) (500mg, 1.2mmol) was added. After stirring at ambient temperature for 1 hour, the mixture was diluted with ethyl acetate (150mL) and treated with 0.26M $Na_2S_2O_3$ solution in saturated aqueous $NaHCO_3$. The organic phase was washed with saturated aqueous NaHCO3 and brine, dried with magnesium sulfate and

evaporated to yield *N*-[(S)-1-(1-Benzooxazol-2-yl-methanoyl)-propyl]-4-morpholin-4-yl-4-oxo-2-benzylsulfonylmethyl-butyramide (377mg) as mixture of diastereomers. The product was purified by flash chromatography on silica gel (hexane/ethyl acetate ratio of 1:2 to 1:4); ^{1}H NMR: (DMSO), 8.85 (d, J=6.2Hz), 8.77 (d, J=6.2Hz), 1H],, 8.00 (d, J=7.7Hz), 7.99 (d, J=7.7Hz), 1H],, 7.90 (d, J=8.2Hz), 7.89 (d, J=8.2Hz), 1H], 7.64 (t, J=7.9Hz, 1H), 7.54 (t, J=7.4Hz, 1H), 7.42-7.34 (m, 5H), 5.25-5.12 (m, 1H), 4.55-4.38 (m, 2H), 3.60-3.28 (m, 10H), 3.12-3.02 (m, 1H), 2.64-2.50 (m, 2H), 2.08-1.91 (m, 1H), 1.82-1.65 (m, 1H), 0.98 (t, J=7.4Hz, 3H); MS: (M^++1) 542;

The following compounds of Formula I were provided by proceeding as in Example 3:

N-[(S)-1-(1-Benzooxazol-2-yl-methanoyl)-pentyl]-4-morpholin-4-yl-4-oxo-2-benzylsulfonylmethyl-butyramide (Compound 30); ^{1}H NMR: (DMSO), 8.84 (d, J=6.4Hz), 8.76 (d, J=6.4Hz), 1H],, 8.00 (d, J=7.7Hz), 7.98 (d, J=7.7Hz), 1H],, 7.89 (d, J=8.2Hz), 7.88 (d, J=8.2Hz), 1H], 7.64 (t, J=7.9Hz, 1H), 7.53 (t, J=7.4Hz, 1H), 7.42-7.34 (m, 5H), 5.30-5.17 (m, 1H), 4.53-4.37 (m, 2H), 3.56-3.26 (m, 10H), 3.12-3.00 (m, 1H), 2.66-2.52 (m, 2H), 2.00-1.86 (m, 1H), 1.76-1.61 (m, 1H), 1.48-1.22 (m, 4H), 0.85 (t, J=6.9Hz, 3H); MS: (M^++1) 570;

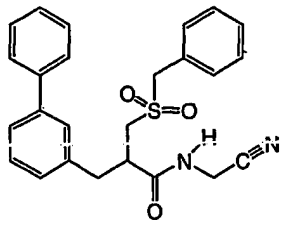
(S)-2,2-Difluoro-4-(4-morpholin-4-yl-4-oxo-2-benzylsulfonylmethyl-butanoylamino)-3-oxo-hexanoic acid dimethylamide (Compound 31); ^{1}H NMR: (DMSO) 8.63-8.57 (m, 1H), 7.43-7.34 (m, 5H), 4.69-4.57 (m, 1H), 4.55-4.41 (m, 2H), 3.59-3.30 (m, 10H), 3.14-3.04 (m, 1H),, 2.98 (s), 2.96 (s), 3H],, 2.90 (s), 2.88 (s), 3H], 2.70-2.58 (m, 2H), 1.90-1.72 (m, 1H), 1.66-1.50 (m, 1H), 0.89 (t, J=6.9Hz, 3H); MS: (M^++1) 546; and

N-[(S)-1-(1-Benzylcarbamoyl-methanoyl)-propyl]-4-morpholin-4-yl-4-oxo-2-benzylsulfonylmethyl-butyramide (Compound 32); ^{1}H NMR: (DMSO) 9.26-9.19 (m, 1H),, 8.56 (d, J=6.7Hz), 8.51 (d, J=6.9Hz), 1H], 7.44-7.19 (m, 10H), 4.96-4.85 (m, 1H), 4.53-4.40 (m, 2H), 4.38-4.22 (m, 2H), 3.57-3.30 (m, 10H), 3.11-2.99 (m, 1H), 2.65-2.52 (m, 2H), 1.86-1.71 (m, 1H), 1.61-1.48 (m, 1H), 0.89 (t, J=7.2Hz, 3H); MS: (M^++1) 558.

EXAMPLE 5

3-Biphenyl-3-yl-*N*-cyanomethyl-2-benzylsulfonylmethyl-propionamide

(Compound 35)



3-Biphenyl-3-yl-2-benzylsulfonylmethyl-propionic acid (300mg, 0.76mmol), prepared as in Reference 9, was combined with EDC (300mg, 1.57mmol), HOBt (300mg, 1.96mmol), and aminoacetonitrile hydrochloride (150mg, 1.6mmol). Dichloromethyl (4mL) was added and then 4-methylmorpholine (0.5mL). The mixture was stirred at ambient temperature for 2 hours. After dilution with ethyl acetate (150mL), the solution was washed with water (30mL), saturated aqueous $NaHCO_3$ solution and brine, dried with magnesium sulfate and evaporated under vacuum. The product, 3-biphenyl-3-yl-*N*-cyanomethyl-2-benzylsulfonylmethyl-propionamide (273mg), was crystallized from ethyl acetate/hexane as a white solid; ^{1}H NMR: (DMSO) 8.87 (t, J=5.5Hz, 1H), 7.68-7.14 (m, 14H), 4.45 (d, J=13.8Hz, 1H), 4.38 (d, J=13.8Hz, 1H), 4.13 (m, 2H), 3.49 (dd, J=9.4Hz, J=14.1Hz, 1H), 3.28-3.11 (m, 1H), 3.04-2.76 (m, 3H). MS: (M^++1) 433.

Proceeding as in Example 5 provided the following compound of Formula I:

3-Biphenyl-4-yl-*N*-cyanomethyl-2-benzylsulfonylmethyl-propionamide (Compound 36); ^{1}H NMR: (DMSO) 8.86 (t, J=5.5Hz, 1H), 7.65 (d, J=7.4Hz, 2H), 7.59 (d, J=7.4Hz, 2H), 7.47 (t, J=7.7Hz, 2H), 7.39-7.24 (m, 8H), 4.47 (d, J=13.8Hz, 1H), 4.40 (d, J=13.8Hz, 1H), 4.13 (m, 2H), 3.48 (dd, J=9.4Hz, J=14.1Hz, 1H), 3.23-3.11 (m, 1H), 3.04-2.75 (m, 3H). MS: (M^++1) 433; and

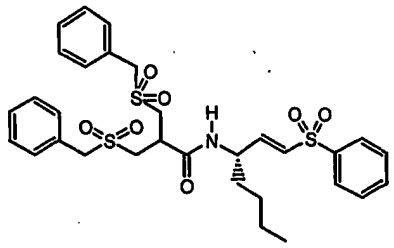
3-(3-Bromo-phenyl)-*N*-cyanomethyl-2-benzylsulfonylmethyl-propionamide (Compound 37); ^{1}H NMR: (DMSO) 8.84 (t, J=5.5Hz, 1H), 7.46-7.14 (m, 9H), 4.46 (d, J=13.8Hz, 1H), 4.40 (d, J=13.8Hz, 1H), 4.10 (m, 2H), 3.46 (dd, J=9.4Hz, J=14.1Hz, 1H),

3.18-3.07 (m, 1H), 2.97 (dd, J=14.1Hz, J=3.4Hz, 1H) 2.88-2.73 (m, 2H). MS: (M^++1) 435/437.

EXAMPLE 6

N-[(S)-1-((E)-2-Benzenesulfonyl-vinyl)-pentyl]-3-benzylsulfonyl-2-benzylsulfonylmethyl-propionamide

(Compound 38)



A mixture of 3-benzylsulfanyl-2-benzylsulfanylmethyl-propionic acid (161 mg), prepared as in Reference 1, 3-benzenesulfonyl-1-n-butylallylamine tosylate (212 mg), HOBt monohydrate (77 mg) and EDC (125 mg) in methylene chloride (6 mL) was treated with N-methylmorpholine (0.25 mL) and stirred at room temperature for 2.5 hours. The reaction mixture was poured into ice cold dilute hydrochloric acid. The product was extracted with ethyl acetate and the organic extracts were washed with aqueous sodium bicarbonate and then with saturated sodium chloride. After drying over magnesium sulfate the solvents were evaporated to give a residue which was crystallized from ethyl acetate/t-butylmethyl ether to yield *N*-[(S)-1-((E)-2-benzenesulfonyl-vinyl)-pentyl]-3-benzylsulfanyl-2-benzylsulfanylmethyl-propionamide (160 mg).

A solution of *N*-[(S)-1-((E)-2-benzenesulfonyl-vinyl)-pentyl]-3-benzylsulfanyl-2-benzylsulfanylmethyl-propionamide (50 mg) in methylene chloride (5 mL) was treated with m-chloroperbenzoic acid (108 mg) and then stirred at room temperature for 65 minutes. The reaction mixture was stirred with aqueous sodium bisulfite and sodium bicarbonate for 85 minutes and then extracted with methylene chloride. The organic extracts were washed with saturated aqueous sodium chloride and dried over magnesium

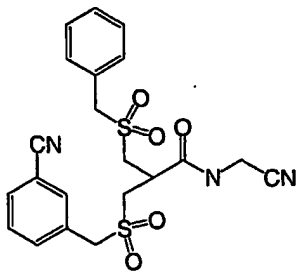
sulfate. Evaporation of the solvent gave a residue which was precipitated from ethyl acetate/t-butylmethyl ether to give *N*-[(S)-1-((E)-2-benzenesulfonyl-vinyl)-pentyl]-3-benzylsulfonyl-2-benzylsulfonylmethyl-propionamide (37 mg); ^{1}H NMR (DMSO): 8.61 (d, J=8Hz, 1H), 7.80 (d, J=7Hz, 2H), 7.69 (t, J=7H, 1H), 7.58 (t, J=8Hz, 2H), 7.38 (m, 10H), 6.86 (m, 2H), 4.6-4.3 (m, 5H), 3.5-3.4 (m, 5H), 1.5 (m, 2H), 1.2 (m, 4H), 0.8 (m, 3H); MS: MH^+ 632.2 (631.17).

Proceeding as in Example 6 provided the following compound of Formula I: N-(3-Benzenesulfonyl-1-phenethyl-allyl)-3-benzylsulfonyl-2-benzylsulfonylmethyl-propionamide (Compound 39); ^{1}H NMR (DMSO): 8.75 (d, J=8Hz, 1H), 7.80 (d, J=7Hz, 2H), 7.70 (t, J=7H, 1H), 7.58 (t, J=8Hz, 2H), 7.4-7.1 (m, 15H), 6.9 (m, 2H), 4.6-4.2 (m, 5H), 3.6-3.3 (m, 5H), 2.6 (m, 2H), 1.8 (m, 2H); MS: MH^+ 680.4 (679.17);

EXAMPLE 7

N-Cyanomethyl-3-(3-cyano-benzylsulfonyl)-2-benzylsulfonyl-methyl-propionamide

(Compound 40)



A mixture of 3-acetylsulfanyl-2-benzylsulfanylmethyl-propionic acid (0.200g), prepared as in Reference 10, HOBt hydrate (0.13g), aminoacetonitrile hydrochloride (0.15g) and EDC (0.26g) was treated with methylene chloride (6 mL) and N-methylmorpholine (0.35 mL). After stirring for 80 minutes at room temperature, the reaction mixture was diluted with ethyl acetate (50mL) and washed sequentially with water, aqueous sodium bicarbonate and saturated aqueous sodium chloride. The solution was dried over magnesium sulfate and evaporated to give thioacetic acid *S*-[3-

benzylsulfanyl-2-(cyanomethyl-carbamoyl)-propyl] ester (0.218 g).

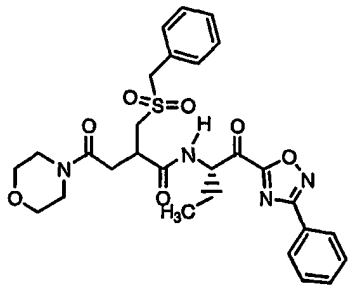
A solution of thioacetic acid *S*-[3-benzylsulfanyl-2-(cyanomethyl-carbamoyl)-propyl] ester (0.105 g) in dimethylformamide (1 mL) and water (0.8 mL) was cooled on ice and treated with 1 N aqueous potassium hydroxide (0.65 mL). 3-Cyanobenzylbromide (0.129 g) in dimethylformamide (0.8 mL) was added. The reaction mixture was allowed to warm to room temperature while stirring overnight. The reaction mixture was then poured into ice water and extracted with ethyl acetate (50 mL) and washed with water and saturated aqueous sodium chloride. The solution was dried over magnesium sulfate and evaporated to give 2-benzylsulfanylmethyl-3-(3-cyano-benzylsulfanyl)-*N*-cyanomethyl-propionamide (0.135 g).

2-Benzylsulfanylmethyl-3-(3-cyano-benzylsulfanyl)-*N*-cyanomethyl-propionamide (0.135 mg) in methanol (10mL) was treated with a solution of Oxone® (0.615g) in water (1.3mL) and the resulting mixture was stirred at room temperature for 45 minutes. The reaction mixture was diluted with water (50mL) and then the methanol was removed by rotary evaporation. The residue was diluted with ethyl acetate and water. The product was extracted with ethyl acetate and the organic layer washed with water and saturated aqueous sodium chloride. The solution was dried over magnesium sulfate and evaporated to give *N*-Cyanomethyl-3-(3-cyano-benzylsulfonyl)-2-benzylsulfonylmethyl-propionamide (0.138 g); ^{1}H NMR: (DMSO) 9.19 (t, J=5Hz, 1H), 7.88 (d, J=8Hz, 1H), 7.82 (s, 1H), 7.72 (d, J=9Hz, 1H), 7.62 (t, J=8Hz, 1H), 7.38 (s, 5H), 4.65 (d, J=14Hz, 1H), 4.58 (d, J=14Hz, 1H), 4.53 (d, J=13Hz, 1H), 4.47 (d, J=13Hz, 1H), 4.17 (d, J=5Hz, 2H), 3.5-3.3 (m, 5H); MS: (M^++1) 460.2; 459.09.

EXAMPLE 8

4-Morpholin-4-yl-4-oxo-2-benzylsulfonylmethyl-*N*-{(S)-1-[1-(3-phenyl-[1,2,4]oxadiazol-5-yl)-methanoyl]-propyl}-butyramide

(Compound 41)

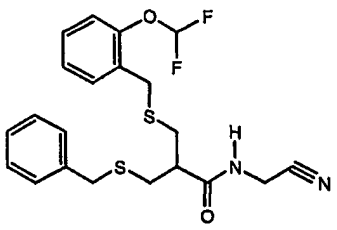


A mixture of (S)-2-amino-1-(3-phenyl-[1,2,4]oxadiazol-5-yl)-butan-1-one, prepared as in Reference 11, 4-morpholin-4-yl-4-oxo-2-benzylsulfonylmethyl-butyric acid (200mg, 0.56mmol), EDC (200mg, 1.05mmol), HOBt (200mg, 1.30mmol), CH_2Cl_2 (4mL) and 4-methylmorpholine (0.5mL) was stirred at ambient temperature for 2 hours. After dilution with ethyl acetate (150mL), the solution was washed with water (30mL), saturated aqueous $NaHCO_3$ solution and brine, dried with $MgSO_4$ and evaporated under vacuum. The crude product was dissolved in dry dichloromethyl (10mL) and 1,1,1,1-triacetoxy-1,1-dihydro-1,2-benziodoxol-3(1H)-one (Dess-Martin periodinane) (500mg, 1.2mmol) was added. After stirring at ambient temperatures for 1 hour, the mixture was diluted with ethyl acetate (150mL) and treated with $Na_2S_2O_3$ solution (0.26M) in saturated aqueous $NaHCO_3$. The organic phase was washed with saturated aqueous $NaHCO_3$ and brine, dried with $MgSO_4$ and evaporated. The product was purified by flash chromatography on silica gel (hexane/ethyl acetate in a 1:2 to 1:4 ratio) to yield 4-Morpholin-4-yl-4-oxo-2-benzylsulfonylmethyl-*N*-{(S)-1-[1-(3-phenyl-[1,2,4]oxadiazol-5-yl)-methanoyl]-propyl}-butyramide (150mg) as mixture of diastereomers; ^{1}H NMR: (DMSO), 9.03 (d, J=5.9Hz), 8.89 (d, J=6.4Hz), 1H], 8.09-8.03 (m, 2H), 7.66-7.55 (m, 3H), 7.42-7.33 (m, 5H), 4.97-4.78 (m, 1H), 4.53-4.35 (m, 2H), 3.58-3.02 (m, 11H), 2.65-2.50 (m, 2H), 2.06-1.90 (m, 1H), 1.83-1.66 (m, 1H), 0.97 (t, J=7.2Hz, 3H); MS: (M^++1) 569.

Example 9

N-Cyanomethyl-2-[2-1,1-difluoro-methoxy)-benzylsulfanylmethyl]-3-benzylsulfanyl-propionamide

(Compound 42):



A mixture of 2-benzylsulfanylmethyl-3-[2-(1,1-difluoromethoxy)-benzyl-sulfanyl]-propionic acid (96 mg, 0.241 mmol)(prepared above in Reference 2), HOBt hydrate (37 mg, 0.24 mmol), aminoacetonitrile hydrochloride (33 mg, 0.36 mmol), EDC (69 mg, 0.36 mmol) and N-methylpyrolidinone (1 mL) was treated with N-methylmorpholine (0.050 mL) and then stirred at room temperature for 3 hours. The reaction mixture was then poured into cold dilute HCl and the product extracted with ethyl acetate, The organic extracts were washed with aqueous sodium bicarbonate then saturated sodium chloride and dried over magnesium sulfate. Evaporation of the solvent then gave N-cyanomethyl-2-[2-1,1-difluoro-methoxy)-benzylsulfanylmethyl]-3-benzylsulfanyl-propionamide (46 mg).

The following compounds of Formula 1 are provided by this method by substitution of 2-benzylsulfanylmethyl-3-[2-(1,1-difluoromethoxy)-benzylsulfanyl]-propionic acid with the appropriate carboxylic acid:

N-Cyanomethyl-3-(2-trifluoromethyl-benzylsulfanyl)-2-(2-trifluoro-methyl-benzylsulfanylmethyl)-propionamide (Compound 43); ^{1}H-NMR ($CDCl_3$) δ: 7.57 (m, 6H); 7.36 (t, J=7.4 Hz, 2H); 6.01 (m, 1H); 4.16 (d, J=5.9 Hz, 2H); 3.86 (s, 4H); 2.70 (m, 4H); 3.35 (m, 1H); MS: (M+) 507.0, M(-) 504.2;

N-Cyanomethyl-3-isobutylsulfanyl-2-isobutylsulfanylmethyl-propionamide (Compound 44); ^{1}H NMR (DMSO): 8.77 (t, J=6 Hz, 1H), 4.5 (d, J=6 Hz, 2H), 2.60 (s, 5H), 2.34 (d, J=7 Hz, 4H), 1.70 (hept, J=7 Hz, 2H), 0.91 (d, J=7Hz, 12H); MS: M(H+) 303.0 (302.15);

N-Cyanomethyl-4-phenylsulfanyl-2-(2-phenylsulfanyl-ethyl)-butyramide (Compound 45); ^{1}H NMR (DMSO): 8.83 (t, J=5Hz, 1H); 7.3 (m, 10H); 4.22 (d, J=6Hz, 2H); 2.90 (m, 4H); 2.65 (m, 1H); 1.85 (m, 2H); 1.72 (m, 2H); MS: M(H+) 370.4

(370.12);

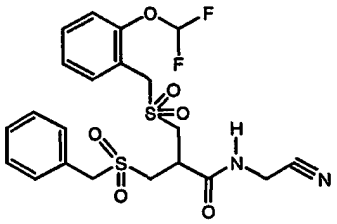
N-Cyanomethyl-3-[2-(1,1-difluoro-methoxy)-benzylsulfanyl]-2-[2-(1,1-difluoro-methoxy)-benzylsulfanylmethyl]-propionamide (Compound 46); ^{1}H NMR (DMSO): 8.88 (t, J=5Hz, 1H); 7.4-7.1 (m, 8H); 7.15 (t, J=74Hz, 2H); 4.18 (t,J=3Hz, 2H); 3.74 (d, J=13Hz, 4H); 2.75 (m, 1H); 2.65-2.5 (m, 4H); MS: M(H+) 504.1 (502.1); and

3-Benzylsulfanyl-2-benzylsulfanylmethyl-*N*-cyanomethyl-propionamide (Compound 47); ^{1}H NMR (DMSO): 8.86 (t, J=6Hz, 1H); 7.26 (m, 10H); 4.20 (d, J=5Hz, 2H); 3.7 (s, 4H); 2.73 (m, 1H); 2.55-2.37 (m, 4H); MS: M(H+) 370.4 (370.12).

Example 10

N-Cyanomethyl-2-[2-1,1-difluoro-methoxy)-benzylsulfonylmethyl]-3-benzylsulfonyl-propionamide

(Compound 48)



A solution of N-cyanomethyl-2-[2-(1,1-difluoro-methoxy)-benzyl-sulfanylmethyl]-3-benzylsulfanyl-propionamide (46 mg) in methanol (5 mL) was treated with Oxone® (184 mg in 2.5 mL of water) and stirred at ambient temperature for 18 hours. An additional portion of Oxone® (166mg in 1.5 mL of water) was added along with more methanol (10 mL) and the reaction mixture was stirred again for 18 hours. Water was added to the reaction mixture and the methanol was removed by rotary evaporation and the product was extracted with ethyl acetate. The organic extracts were washed with aqueous sodium bicarbonate then saturated sodium chloride and dried over magnesium sulfate. Evaporation of the solvent then gave N-cyanomethyl-2-[2-(1,1-difluoro-methoxy)-benzylsulfonylmethyl]-3-phenyl-methylsulfonyl-propionamide (67 mg); ^{1}H NMR (DMSO): 9.19 (t, J =5 Hz, 1H), 7.47 (m, 2H), 7.38 (s, 5H), 7.25 (m, 2H), 7.13 (t, J=74 Hz,

1H), 4.54 (s, 2H), 4.53 (d, J=14 Hz, 1H), 4.46 (d, J = 14 Hz, 1H), 4.16 (d, J = 5 Hz, 2H), 3.5 (m, 5H); MS: M(H+) 501.0 (500.09).

The following compounds of Formula 1 are provided by this method by substitution of N-cyanomethyl-2-[2-(1,1-difluoro-methoxy)-benzyl-sulfanylmethyl]-3-benzylsulfanyl-propionamide with the appropriate N-cyanomethyl propionamide:

N-Cyanomethyl-3-(2-trifluoromethyl-benzylsulfonyl)-2-(2-trifluoromethyl-benzylsulfonylmethyl)-propionamide.(Compound 49); ^{1}H-NMR (DMSO) δ: 9.23 (t, J=5.4 Hz, 1H); 7.79 (m, 2H); 7.67 (m, 6H); 4.72 (m, 4H); 4.18 (t, J=2.7 Hz, 2H); 3.53-3.76 (m, 5H); MS: M(+) 539.0; M(-) 536.6;

4-Benzenesulfonyl-2-(2-benzenesulfonyl-ethyl)-*N*-cyanomethyl-butyramide (Compound 50); ^{1}H NMR (DMSO): 8.67 (t, J=5Hz, 1H); 7.85 (m, 4H); 7.73 (m, 2H); 7.64 (m, 4H); 4.06 (m, 2H); 3.12 (m, 4H); 2.4 (m, 1H); 1.66 (m, 4H); MS: M(H+) 435.2 (434.10);

N-Cyanomethyl-3-[2-(1,1-difluoro-methoxy)-benzylsulfonyl]-2-[2-(1,1-difluoro-methoxy)-benzylsulfonylmethyl]-propionamide (Compound 51); ^{1}H NMR (DMSO): 9.17 (t, J=5Hz, 1H); 7.5-7.4 (m, 4H); 7.3-7.2 (m, 4H); 7.12 (t, J=74Hz, 2H); 4.54 (s, 4H); 4.15 (m, 2H); 3.6-3.4 (m, 5H); MS: M(H+) 567.2 (566.08); and

N-Cyanomethyl-3-benzylsulfonyl-2-benzylsulfonylmethyl-propionamide (Compound 52); ^{1}H NMR (DMSO): 9.19 (t, J=5Hz, 1H); 7.38 (s, 10H); 4.53 (d, J=14Hz, 2H); 4.46 (d,J=14Hz, 2H); 4.17 (t, J=3Hz, 2H); 3.5-3.3 (m, 5H); MS: M(H+) 435.2 (434.1).

The following compounds of Formula I are provided by the methods described in this application:

N-[(S)-1-(1-Benzylcarbamoyl-methanoyl)-propyl]-3-benzylsulfonyl-2-benzylsulfonylmethyl-propionamide (Compound 53); ^{1}H-NMR (DMSO) δ: 9.27 (t, J=6Hz, 1H); 8.89 (d, J=6 Hz, 1H); 7.4-7.2 (m, 15H); 5 (m, 1H); 4.5 (m, 4H); 4.3 (m, 2H); 3.67 (m, 1H); 3.5-3.2 (m, 4H), 1.8 (m, 1H)1.6 (m, 1H); 0.91 (t, J=7Hz, 3H); MS: (M+) 599.0, M(-) 598.18;

N-[(S)-1-(1-Benzooxazol-2-yl-methanoyl)-butyl]-2-[2-(1,1-difluoro-methoxy)-benzylsulfonylmethyl]-3-benzylsulfonyl-propionamide (Compound 54); ^{1}H-NMR (DMSO) δ: 9.1 (t, J=6Hz, 1H); 7.99 (d, J=8Hz, 1H); 7.88 (d, J=8Hz, 1H); 7.7-7.2 (m, 14H); 5.35 (m, 1H); 4.6-4.4 (m, 5H); 3.7-3.3 (m, 5H); 1.9 (m, 1H), 1.7 (m, 1H)1.45 (m, 2H); 0.90 (t, J=7Hz, 3H); MS: (M+) 599.0, M(-) 598.18;

N-Cyanomethyl-3-(2-methyl-propane-1-sulfonyl)-2-(2-methyl-propane-1-sulfonylmethyl)-propionamide (Compound 55); ^{1}H-NMR (DMSO) δ: 9.13 (t, J=5Hz, 1H); 4.14 (m, 2H); 3.5-3.3 (m, 5H), 3.1-2.95 (m, 4H), 2.17 (h, J=7Hz, 2H)1.01 (d, J=7Hz, 12H); MS: (M+) 367.0, 366.13;

Acetic acid (2S,3S)-3-(4-morpholin-4-yl-4-oxo-2-benzylsulfonylmethyl-butanoylamino)-4-oxo-azetidin-2-yl ester (Compound 58); ^{1}H NMR: (DMSO) 9.19 (d, J=5.9Hz, 1H),, 8.94 (d, J=7.6Hz), 8.90 (d, J=7.6Hz), 1H], 7.42-7.35 (m, 5H), 5.70 (m, 1H), 4.60 (m, 1H), 4.56-4.40 (m, 2H), 3.58-3.06 (m, 11H), 2.70-2.50 (m, 2H), 2.07 (s, 3H); MS: (M^++1) 482;

N-Cyanomethyl-3-(2-methyl-thiazol-4-ylmethylsulfonyl)-2-benzyl-sulfonylmethyl-propionamide (Compound 59); ^{1}H NMR (DMSO): 9.14 (t, J=5 Hz, 1H), 7.52 (s, 1H), 7.38 (s, 5H), 4.64 (s, 2H), 4.53 (d, J=14 Hz, 1H), 4.46 (d, J = 14 Hz, 1H), 4.16 (d, J = 5 Hz, 2H), 3.5 (m, 5H), 2.63 (s, 3H); M=455.06, M(H+)=456.0;

N-(3-Benzenesulfonylamino-2-oxo-propyl)-4-morpholin-4-yl-4-oxo-2-benzylsulfonylmethyl-butyramide (Compound 60); ^{1}H NMR: (DMSO) 8.46 (t, J=5.2Hz, 1H), 7.97 (t, J=5.7Hz, 1H), 7.79 (d, J=7Hz, 2H), 7.66-7.52 (m, 3H), 7.44-7.36 (m, 5H), 4.56-4.43 (m, 2H), 3.94 (d, J=5.2Hz, 2H), 3.84 (d, J=5.7Hz, 2H), 3.59-3.04 (m, 11H), 2.75-2.55 (m, 2H); MS: (M^++1) 566;

3-Biphenyl-3-yl-*N*-cyanomethyl-2-[2-(1,1-difluoro-methoxy)-benzyl-sulfonylmethyl]-propionamide (Compound 61); ^{1}H NMR: (DMSO) 8.86 (t, J = 5.4 Hz, 1H), 7.70-7.10 (m, 13H), 7.12 (t, J = 73.7 Hz, 1H), 4.46 (s, 2H), 4.13 (m, 2H), 4.10 (d, J = 5.6Hz, 2H), 3.57 (m, 1H), 3.20-3.00 (m, 2H), 3.00-2.80 (m, 2H); MS: (M^++1) 499;

(3'-{2-(Cyanomethyl-carbamoyl)-3-[2-(1,1-difluoro-methoxy)-benzyl-sulfonyl]-propyl}-biphenyl-4-yl)-carbamic acid ethyl ester (Compound 62); ^{1}H NMR: (DMSO) 9.70 (s, 1H), 8.84 (t, J = 5.4 Hz, 1H), 7.55 (s, 4H), 7.50-7.15 (m, 8H), 7.11 (t, J = 73.7 Hz, 1H),

4.45 (s, 2H), 4.13 (m, 2H), 4.09 (d, J = 5.5Hz, 2H), 3.56 (m, 1H), 3.20-3.00 (m, 2H), 2.95-2.75 (m, 2H), 1.24 (t, J = 6.9 Hz, 3H); MS: (M^++1) 586;

N-Cyanomethyl-2-[2-(1,1-difluoro-methoxy)-benzylsulfonylmethyl]-3-(4'-methylsulfonylamino-biphenyl-3-yl)-propionamide (Compound 63); ^{1}H NMR: (DMSO) 9.77 (s, 1H), 8.79 (t, J = 5.4 Hz, 1H), 7.57 (d, J=8.6, 2H), 7.50-7.00 (m, 8H), 7.27 (d, J=8.6 Hz, 2H), 7.06 (t, J = 73 Hz, 1H), 4.40 (s, 2H), 4.04 (d, J = 5.6Hz, 2H), 3.51 (m, 1H), 3.20-3.00 (m, 2H), 2.90-2.70 (m, 2H); MS: (M^++1) 592;

3-(3-Bromo-phenyl)-*N*-cyanomethyl-2-[2-(1,1-difluoro-methoxy)-phenyl-methylsulfonylmethyl]-propionamide (Compound 64); ^{1}H NMR: (DMSO) 8.80 (t, J = 5.4 Hz, 1H), 7.50-7.35 (m, 4H), 7.35-7.15 (m, 4H), 7.13 (t, J = 73 Hz, 1H), 4.46 (s, 2H), 4.06 (d, J = 5.4Hz, 2H), 3.53 (m, 1H), 3.20-3.00 (m, 2H), 2.90-2.70 (m, 2H); MS: (M^++1) 501;

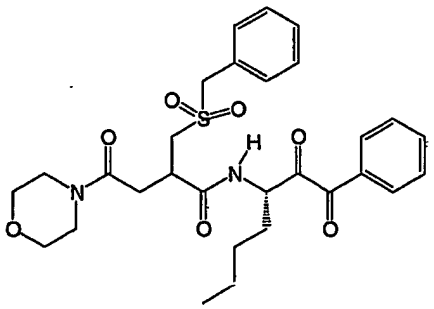
N-Cyanomethyl-2-((E)-3-phenyl-allyl)-3-benzylsulfonyl-propionamide (Compound 65); ^{1}H NMR: (DMSO) 8.85 (t, J = 5.4 Hz, 1H), 7.40-7.10 (m, 10H), 6.35 (d, J=15 Hz, 1H), 6.15-5.95 (m, 1H), 4.41 (s, 2H), 4.08 (d, J = 5.4Hz, 2H), 3.56-3.35 (m, 2H), 3.25-2.90 (m, 3H); MS: (M^++1) 383; and

N-Cyanomethyl-3-benzylsulfonyl-2-(3-phenyl-propyl)-propionamide (Compound 66); ^{1}H NMR: (DMSO) 8.91 (t, J = 5.4 Hz, 1H), 7.45-7.10 (m, 10H), 4.41 (s, 2H), 4.08 (d, J = 5.4Hz, 2H), 3.30-2.80 (m, 3H), 2.34 (t, J = 7.4 Hz, 2H), 2.22-2.12 (m, 2H), 2.10-1.85 (m, 2H); MS: (M^++1) 385.

EXAMPLE 11

4-Morpholin-4-yl-4-oxo-*N*-[1-(2-oxo-2-phenyl-acetyl)-pentyl]-2-benzylsulfonylmethyl-butyramide

(Compound 67)



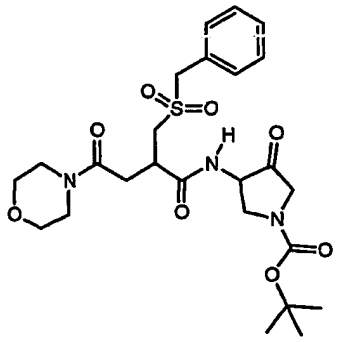
2-Amino-1-(2-phenyl-[1,3]dithian-2-yl)-hexan-1-ol, prepared as in reference 12, was coupled with 4-morpholin-4-yl-4-oxo-2-benzylsulfonylmethyl-butyric acid, according to the procedure outlined in example 8, resulting in *N*-{1-[Hydroxy-(2-phenyl-[1,3]dithian-2-yl)-methyl]-pentyl}-4-morpholin-4-yl-4-oxo-2-benzylsulfonyl-methyl-butyramide as a mixture of diastereomers.

N-{1-[Hydroxy-(2-phenyl-[1,3]dithian-2-yl)-methyl]-pentyl}-4-morpholin-4-yl-4-oxo-2-benzylsulfonylmethyl-butyramide (0.23 g, 0.35 mmol) in 9mL acetonitrile and 2.25mL water at 23°C was mixed with finely ground $HgCl_2$ (212 mg, 0.78 mmol) and finely ground calcium carbonate (90 mg, 0.89 mmol). The mixture was stirred for 25 minutes and then diluted with ethyl acetate. Water was added and the pH lowered to 6 by the addition of 1N HCl. After separation, the organic layer was washed sequentially with water and brine (twice). The organics were dried with magnesium sulfate, concentrated and chromatographed on silica gel using a hexane-ethyl acetate gradient to afford 150 mg of *N*-[1-(1-Hydroxy-2-oxo-2-phenyl-ethyl)-pentyl]-4-morpholin-4-yl-4-oxo-2-phenyl-methylsulfonylmethyl-butyramide as a mixture of diastereomers (76% yield).

N-[1-(1-Hydroxy-2-oxo-2-phenyl-ethyl)-pentyl]-4-morpholin-4-yl-4-oxo-2-benzylsulfonylmethyl-butyramide was oxidized by methods described in the above examples resulting in 4-morpholin-4-yl-4-oxo-*N*-[1-(oxo-phenyl-acetyl)-pentyl]-2-benzylsulfonylmethyl-butyramide as a mixture of diastereomers; ^{1}HNMR: (DMSO), 8.9 (d, J = 6 Hz), 1/2H diastereomeric],, 8.86 (d, J = 6 Hz), 1/2H diastereomeric], 7.89-7.84 (m, 2H), 7.7-7.67 (m, 1H), 7.56-7.5 (m, 2H), 7.4-7.3 (m, 5H), 4.56-4.54 (m, 1H), 4.41-4.35 (m, 2H), 3.4-4.6 (m, 4H), 3.35-3.25 (m, 4H), 3.2-3.1 (m, 2H), 2.99 –2.95 (m, 1H), 1.9-1.6 (m, 2H), 1.5-1.2 (m, 6H), 1.0-0.9 (m, 3H); MS: (M^+ + 1) 557.

EXAMPLE 12

3-(4-Morpholin-4-yl-4-oxo-2-benzylsulfonylmethyl-butyrylamino)-4-oxo-pyrrolidine-1-carboxylic acid tert-butyl ester



(Compound 68)

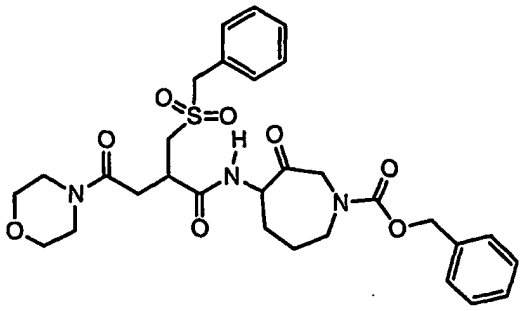
4-Morpholin-4-yl-4-oxo-2-benzylsulfonylmethyl-butyric acid (120mg, 0.34mmol), 3-amino-4-hydroxy-pyrrolidine-1-carboxylic acid tert-butyl ester (150mg, 0.74mmol), prepared as in reference 13, EDC (0.3g, 1.6mmol), and HOBt (150mg, 0.96mmol) were combined. Dichloromethyl (10mL) was added and then 4-methylmorpholine (0.5mL). The mixture was stirred at ambient temperature for 2hours. After dilution with ethyl acetate (200mL) the solution was washed with 1N aqueous HCl (50mL), saturated aqueous $NaHCO_3$ (50mL) and brine (50mL), dried with $MgSO_4$ and evaporated under vacuum. The crude 3-hydroxy-4-(4-morpholin-4-yl-4-oxo-2-benzylsulfonylmethyl-butyrylamino)-pyrrolidine-1-carboxylic acid tert-butyl ester was dissolved in DMSO (5mL). Triethylamine (0.5mL) and then SO_3 pyridine complex (150mg) were added and the mixture was stirred at ambient temperature for 3 hours. After dilution with ethyl acetate (100mL), the solution was washed with water (50mL) and brine, dried with $MgSO_4$ and evaporated under vacuum. The residue was purified by flash chromatography on silica gel. Eluent: 5% methanol in ethyl acetate. Yield: 40mg 3-(4-morpholin-4-yl-4-oxo-2-benzylsulfonylmethyl-butyrylamino)-4-oxo-pyrrolidine-1-carboxylic acid tert-butyl ester as white solid as mixture of diastereomers; ^1H NMR: (DMSO) 8.80-8.66 (m, 1H), 7.42-

7.34 (m, 5H), 4.52-4.41 (m, 2H), 4.34-4.20 (m, 1H), 3.98-3.88 (m, 1H), 3.82 (d, J=18.5Hz, 1H), 3.70-3.05 (m, 13H), 2.70-2.52 (m, 2H), 1.41 (s, 9H); MS: $(M+H)^+$ 538.

EXAMPLE 13

4-(4-Morpholin-4-yl-4-oxo-2-benzylsulfonylmethyl-butyrylamino)-3-oxo-azepane-1-carboxylic acid benzyl ester

(Compound 69)



Sodium hydride (60% in mineral oil, 10g, 250mmol) was suspended in dry DMF. Allyl-carbamic acid benzyl ester (19.1g, 100mmol) was added drop wise at ambient temperature. After stirring for 5 minutes, 5-bromo-1-pentene (25g, 168mmol) was added drop wise. Stirring was continued at 50°C for 1 hour. The reaction was quenched with water and then partitioned between diethyl ether and water. The ether layer was washed with water and brine, dried with $MgSO_4$ and evaporated under vacuum. Flash chromatography (ethyl acetate/hexane 1:9) gave 15.5g allyl-pent-4-enyl-carbamic acid benzyl ester.

Allyl-pent-4-enyl-carbamic acid benzyl ester (15.5g, 59.8mmol) was dissolved in dichloromethyl and bis(tricyclohexylphosphine)benzylidene ruthenium(IV) dichloride (1g) was added. The mixture was refluxed under a nitrogen atmosphere until TLC analysis showed complete reaction. The solvent was evaporated under vacuum and the residue was purified by flash chromatography (ethyl acetate/hexane 1:9). Yield: 7.8g 2,3,4,7-Tetrahydro-azepine-1-carboxylic acid benzyl ester.

To a solution of 2,3,4,7-tetrahydro-azepine-1-carboxylic acid benzyl ester (4.5g, 19.45mmol) in dichloromethyl (50mL) was added m-chloroperbenzoic acid (60mmol).

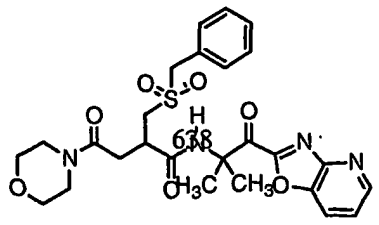
The mixture was stirred at ambient temperature for 16 hours. Saturated aqueous K_2CO_3 solution was added and the mixture was extracted with dichloromethyl. The combined organic layers were washed with saturated aqueous $NaHCO_3$ and brine, dried with $MgSO_4$ and evaporated under vacuum. The crude epoxide was dissolved in a 8:1 methanol/water mixture (100mL). Ammonium chloride (3.2g, 60mmol) and sodium azide (3.9g, 60mmol) was added and the mixture was heated at 60°C for 48 hours. Most of the solvent was removed under vacuum. The residue was extracted with ethyl acetate. The combined organic layers were washed with saturated aqueous $NaHCO_3$ (200mL) and brine (200mL), dried with $MgSO_4$ and evaporated under vacuum. Flash chromatography of the residue (hexane/ethyl acetate 3:1) gave 3.3g of 4-azido-3-hydroxy-azepane-1-carboxylic acid benzyl ester.

To a solution of 4-azido-3-hydroxy-azepane-1-carboxylic acid benzyl ester (3.3g, 11.37mmol) in methanol (50mL) was added triethylamine (5mL) and 1,3-propanedithiol (3.42mL, 35mmol). The mixture was stirred at ambient temperature until TLC analysis showed complete consumption of the starting material. A white precipitate was removed by filtration and the filtrate was evaporated to dryness. The residue was triturated with a 1:1 hexane/diethyl ether mixture to remove excess dithiol and dried under vacuum.

The crude 4-amino-3-hydroxy-azepane-1-carboxylic acid benzyl ester was coupled to 4-morpholin-4-yl-4-oxo-2-benzylsulfonylmethyl-butyric acid and oxidized, as described above, to yield 4-(4-morpholin-4-yl-4-oxo-2-benzylsulfonylmethyl-butyrylamino)-3-oxo-azepane-1-carboxylic acid benzyl ester; ^{1}H NMR: (DMSO) 8.46-8.42 (m, 1H), 7.44-7.24 (m, 10H), 5.18-5.04 (m, 2H), 4.52-4.33 (m, 4H), 4.04-3.76 (m, 2H), 3.58-3.30 (m, 11H), 3.11-3.03 (m, 1H), 2.96-2.78 (m, 1H), 2.72-2.57 (m, 1H), 1.84-1.55 (m, 4H); MS: $(M+H)^+$ 600.

EXAMPLE 14

N-(1,1-Dimethyl-2-oxazolo[4,5-b]pyridin-2-yl-2-oxo-ethyl)-4-morpholin-4-yl-4-oxo-2-benzylsulfonylmethyl-butyramide



(Compound 70)

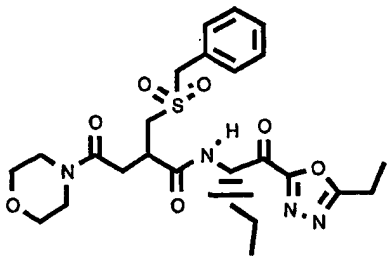
To a stirred mixture of 4-morpholin-4-yl-4-oxo-2-benzylsulfonylmethyl-butyric acid (142mg, 0.4mmol), 2-amino-2-methyl-1-oxazolo[4,5-b]pyridin-2-yl-propan-1-one TFA salt (165mg), prepared as in reference 14, and HOBt (73mg, 0.45mmol) in $MeCl_2$ (5ml) was added EDC (115mg, 0.6mmol) and N-methylmorpholine (0.25ml) at room temperature. After stirring for 14 hours, the reaction mixture was extracted with ethyl acetate. The organic layer was washed with saturated $NaHCO_3$, brine, dried with $MgSO_4$ and concentrated. The residue was purified by silica gel column chromatography to yield 92 mg of *N*-{1-[(5-Ethyl-[1,3,4]oxadiazol-2-yl)-hydroxy-methyl]-butyl}-4-morpholin-4-yl-4-oxo-2-benzylsulfonylmethyl-butyramide.

This amide was treated with Dess-Martin periodinane (125.6mg, 0.254mmol) at room temperature. After stirring for 1 hour, 5ml of saturated $Na_2S_2O_3$-$NaHCO_3$ were added. After a further 0.5 hours, the reaction mixture was extracted with ethyl acetate, washed with brine, dried with $MgSO_4$ and concentrated. The residue was purified with silica gel column chromatography to yield 31 mg of *N*-(1,1-dimethyl-2-oxazolo[4,5-b]pyridin-2-yl-2-oxo-ethyl)-4-morpholin-4-yl-4-oxo-2-benzylsulfonylmethyl-butyramide; H^1 NMR(DMSO-d): 9.36(1H, s, NH), 8.68(1H, d, J=4.7Hz), 8.34(1H, d, J=8.42Hz), 7.62(1H, dd, J=4.7Hz, J=8.42Hz), 7.4-7.4(5H, m), 4.41-4.3(2H, s), 3.5-3(12H, m), 2.2-2.1(1H, m), 1.6(3H, s), 1.51(3H, s); MS: 541.4(M-1), 543.4(M+1).

EXAMPLE 15

N-[1-(5-Ethyl-[1,3,4]oxadiazole-2-carbonyl)-butyl]-4-morpholin-4-yl-4-oxo-2-benzylsulfonylmethyl-butyramide

(Compound 71)

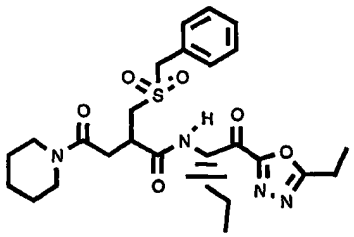


To a stirred mixture of 4-morpholin-4-yl-4-oxo-2-benzylsulfonylmethyl-butyric acid (177.7mg, 0.5mmol), 2-amino-1-(5-ethyl-1,3,4-oxadiazole-2-yl)-1-pentanol HCl salt (117.5mg), and HOBt (91.8mg, 0.6mmol) in $MeCl_2$ (5ml), was added EDC (144mg, 0.75mmol) and N-methylmorpholine (0.3ml) at room temperature. After stirring for 14 hours, the reaction mixture was extracted with ethyl acetate. The organic layer was washed with saturated $NaHCO_3$, brine, dried with $MgSO_4$ and concentrated to yield 240 mg of crude product (MS: 536(M-1), 538.4(M+1)). Without further purification, the crude product was treated with Dess-Martin periodinane (334mg, 0.67mmol) at room temperature in 5mL of $MeCl_2$. After stirring for 1 hour, 5mls of saturated $Na_2S_2O_3$-$NaHCO_3$ were added. After a further 0.5 hours, the reaction mixture was extracted with ethyl acetate, washed with brine, dried with $MgSO_4$ and concentrated. The residue was purified with silica gel column chromatography to yield 110 mg of N-[1-(5-ethyl-[1,3,4]oxadiazole-2-carbonyl)-butyl]-4-morpholin-4-yl-4-oxo-2-benzylsulfonylmethyl-butyramide; H^1 NMR(DMSO-d): 8.84(1/2H, d, NH, diastereomeric), 8.78(1/1H, d, NH, diastereomeric), 7.45-7.2(5H, m), 5.05-4.9(1H, m), 4.48-4.3(2H,m), 3.6-3.4(4H, m), 3.4-3.2(4H, m), 3.1-2.4(6H, m), 1.9-1.75(1H, m), 1.7-1.55(2H, m), 1.25-1.2(2H, m), 1.2-1.1(3H, m), 0.9-0.8(3H, m); MS: 534M-1), 535.8(M+1).

EXAMPLE 16

N-[1-(5-Ethyl-[1,3,4]oxadiazole-2-carbonyl)-butyl]-4-oxo-2-benzylsulfonyl-methyl-4-piperidin-1-yl-butyramide

(Compound 72)



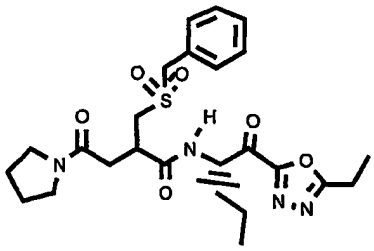
To a stirred mixture 4-oxo-2-benzylsulfonylmethyl-4-piperidin-1-yl-butyric acid (176.5mg, 0.5mmol), 2-amino-1-(5-ethyl-1,3,4-oxadiazole-2-yl)-1-pentanol HCl salt (117.5mg), and HOBt (91.8mg, 0.6mmol) in $MeCl_2$ (5ml), was added EDC (144mg, 0.75mmol) and N-methylmorpholine (0.3ml) at room temperature. After stirring for 14 hours, the reaction mixture was extracted with ethyl acetate. The organic layer was washed with saturated $NaHCO_3$, brine, dried with $MgSO_4$ and concentrated to yield 270mg of crude product; MS: 534.1(M-1), 535.7(M+1).

The amide was then treated with Dess-Martin periodinane (378.7mg, 0.675mmol) at room temperature in 5 ml of $MeCl_2$. After stirring for 1 hour, 5ml of saturated $Na_2S_2O_3$-$NaHCO_3$ were added. After a further 0.5 hours, the reaction mixture was extracted with ethyl acetate, washed with brine, dried with $MgSO_4$ and concentrated. The residue was purified with silica gel column chromatography to yield 165 mg of *N*-[1-(5-Ethyl-[1,3,4]oxadiazole-2-carbonyl)-butyl]-4-oxo-2-benzyl-sulfonyl-methyl-4-piperidin-1-yl-butyramide; H^1 NMR (DMSO-d): 8.85(1/2H, d, NH, diastereomeric), 8.78(1/2, d, NH, diastereomeric), 7.4-7.2(5H, m), 5.1-4.9(1H, m), 4.5-4.3(2H,m), 3.5-3.2(8H, m), 3.1-2.6(1H, m), 2.9(2H, m), 1.9-1.6(2H, m), 1.6-1.2(8H, m), 1.24(3H, m), 0.9-0.8(3H, m); MS: 531.6(M-1), 533.4(M+1).

EXAMPLE 17

N-[1-(5-Ethyl-[1,3,4]oxadiazole-2-carbonyl)-butyl]-4-oxo-2-benzylsulfonyl-methyl-4-pyrrolidin-1-yl-butyramide

(Compound 73)

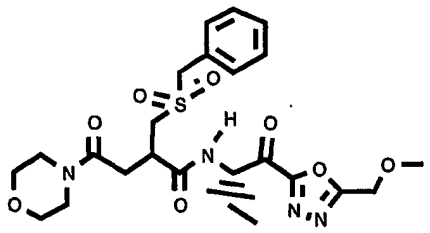


To a stirred mixture 4-cyclopentyl-4-oxo-2-benzylsulfonylmethyl-butyric acid (169.5mg, 0.5mmol), 2-amino-1-(5-ethyl-1,3,4-oxadiazole-2-yl)-1-pentanol HCl salt (117.5mg), and HOBt (91.8mg, 0.6mmol) in $MeCl_2$ (5ml), was added EDC (144mg, 0.75mmol) and N-methylmorpholine (0.3ml) at room temperature. After stirring for 14 hours, the reaction mixture was extracted with ethyl acetate. The organic layer was washed with saturated $NaHCO_3$, brine, dried with $MgSO_4$ and concentrated to yield 240 mg of crude product. The crude product was treated with Dess-Martin periodinane (343mg, 0.693mmol) at room temperature in 5mls of $MeCl_2$. After stirring for 1 hour, 5mls of saturated $Na_2S_2O_3$-$NaHCO_3$ were added. After a further 0.5 hours, the reaction mixture was extracted with ethyl acetate, washed with brine, dried with $MgSO_4$ and concentrated. The residue was purified with silica gel column chromatography to yield 145 mg of *N*-[1-(5-Ethyl-[1,3,4]oxadiazole-2-carbonyl)-butyl]-4-oxo-2-benzylsulfonyl-methyl-4-pyrrolidin-1-yl-butyramide; H^1 NMR(DMSO-d): 8.85(1/2H, d, NH, diastereomeric), 8.78(1/2H, d, NH, diastereomeric), 7.5-7.3(5H, m), 5.1-4.95(1H, m), 4.5-4.3(2H,m), 3.5-3.2(8H, m), 3.2-3(1H, m), 2.82(2H, m), 2-1.8(6H, m), 1.6-1.3(2H, m), 1.24(3H, m), 0.9-0.8(3H, m); MS: 518.2(M-1), 519.7(M+1).

EXAMPLE 18

N-[1-(5-Methoxymethyl-[1,3,4]oxadiazole-2-carbonyl)-propyl]-4-morpholin-4-yl-4-oxo-2-benzylsulfonylmethyl-butyramide

(Compound 74)



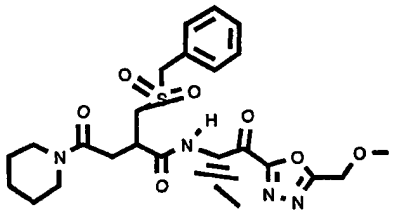
To a stirred mixture of 4-morpholin-4-yl-4-oxo-2-benzylsulfonylmethyl-butyric acid (230mg, 0.65mmol), 2-amino-1-(5-methoxymethyl-[1,3,4]oxadiazol-2-yl)-butan-1-one TFA salt (204mg), prepared as in reference 15, and HOBt (119mg, 0.78mmol) in $MeCl_2$ (5ml), was added EDC (187mg, 0.98mmol) and N-methylmorpholine (0.35ml) at room temperature. After stirring for 14 hours, the reaction mixture was extracted with ethyl acetate. The organic layer was washed with saturated $NaHCO_3$, brine, dried with $MgSO_4$ and concentrated to yield 82mg of *N*-{1-[Hydroxy-(5-methoxymethyl-[1,3,4]oxadiazol-2-yl)-methyl]-propyl}-4-morpholin-4-yl-4-oxo-2-benzylsulfonyl-methyl-butyramide; MS: 537.6(M-1), 539.8(M+1).

This amide then was treated with Dess-Martin periodinane (111mg, 0.149mmol) at room temperature. After stirring for 1 hour, 5mls of saturated $Na_2S_2O_3$-$NaHCO_3$ was added. After a further 0.5 hours, the reaction mixture was extracted with ethyl acetate, washed with brine, dried with $MgSO_4$ and concentrated. The residue was purified with silica gel column chromatography to yield 13mgs of *N*-[1-(5-Methoxymethyl-[1,3,4]oxadiazole-2-carbonyl)-propyl]-4-morpholin-4-yl-4-oxo-2-benzylsulfonyl-methyl-butyramide; H^1 NMR($CDCl_3$): 7.8, 7.5(1H, d,d NH, diastereomeric), 7.4-7.2(5H, m), 5.3-5.1(1H, m), 4.6(2H, s, OCH_2), 4.3-4.1(3H, m), 3.8-3.1(13H, m), 3-2.4(2H, m), 2.2-1.5(2H, m), 0.95(3H, t); MS: 535.7(M-1), 537.5(M+1).

EXAMPLE 19

N-[1-(5-Methoxymethyl-[1,3,4]oxadiazole-2-carbonyl)-propyl]-4-oxo-2-benzylsulfonylmethyl-4-piperidin-1-yl-butyramide

(Compound 75)



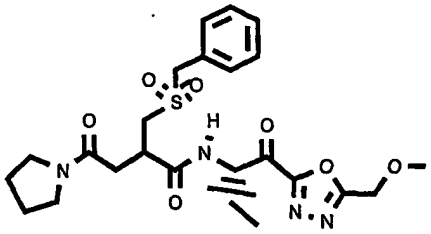
To a stirred mixture of 4-oxo-2-benzylsulfonylmethyl-4-piperidin-1-yl-butyric acid (229mg, 0.65mmol), 2-amino-1-(5-methoxymethyl-1,3,4-oxadiazole-2-yl)-1-propanol TFA salt (204mg), prepared as in reference 15, and HOBt (119mg, 0.78mmol) in $MeCl_2$ (5ml), was added EDC (187mg, 0.98mmol) and N-methylmorpholine (0.35ml) at room temperature. After stirring for 14 hours, the reaction mixture was extracted with ethyl acetate. The organic layer was washed with saturated $NaHCO_3$, brine, dried with $MgSO_4$ and concentrated to yield 130 mg of *N*-{1-[hydroxy-(5-methoxymethyl-[1,3,4]oxadiazol-2-yl)-methyl]-propyl}-4-oxo-2-benzylsulfonylmethyl-4-piperidin-1-yl-butyramide; MS: 535.4(M-1), 537.7(M+1).

The amide then was treated with Dess-Martin periodinane (180mg, 0.364mmol) at room temperature. After stirring for 1 hour, 5mls of saturated $Na_2S_2O_3$-$NaHCO_3$ were added. After a further 0.5 hours, the reaction mixture was extracted with ethyl acetate, washed with brine, dried with $MgSO_4$ and concentrated. The residue was purified with silica gel column chromatography to yield 26mgs of *N*-[1-(5-Methoxymethyl-[1,3,4]oxadiazole-2-carbonyl)-propyl]-4-oxo-2-benzylsulfonylmethyl-4-piperidin-1-yl-butyramide; H^1 NMR($CDCl_3$): 8, 7.7(1H, d,d, NH, diastereomeric), 7.4-7.2(5H, m), 5.3-5.1(1H, m), 4.6(2H, s, OCH_2), 4.3-4.1(3H, m), 3.8-3.2(9H, m), 3-2.4(2H, m), 2.2-1.4(8H, m), 0.95(3H, t); MS: 535.7(M+1).

EXAMPLE 20

N-[1-(5-Methoxymethyl-[1,3,4]oxadiazole-2-carbonyl)-propyl]-4-oxo-2-benzylsulfonylmethyl-4-pyrrolidin-1-yl-butyramide

(Compound 76)



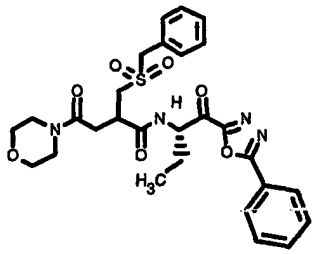
To a stirred mixture of 4-oxo-2-benzylsulfonylmethyl-4-pyrrolidin-1-yl-butyric acid (220mg, 0.65mmol), 2-amino-1-(5-methoxymethyl-1,3,4-oxadiazole-2-yl)-1-propanol TFA salt (204mg), prepared as in reference 15, and HOBt (119mg, 0.78mmol) in $MeCl_2$ (5ml), was added EDC (187mg, 0.98mmol) and *N*-methylmorpholine (0.35ml) at room temperature. After stirring for 14 hours, the reaction mixture was extracted with ethyl acetate. The organic layer was washed with saturated $NaHCO_3$, brine, dried with $MgSO_4$ and concentrated to yield 84 mg of *N*-{1-[Hydroxy-(5-methoxymethyl-[1,3,4]oxadiazol-2-yl)-methyl]-propyl}-4-oxo-2-benzylsulfonylmethyl-4-pyrrolidin-1-yl-butyramide. Without further purification, the crude product was used for next reaction; MS: 521.6(M-1), 523.2(M+1).

This amide was treated with Dess-Martin periodinane (114mg, 0.153mmol) at room temperature. After stirring for 1 hour, 5mls of saturated $Na_2S_2O_3$-$NaHCO_3$ were added. After a further 0.5 hours, the reaction mixture was extracted with ethyl acetate, washed with brine, dried with $MgSO_4$ and concentrated. The residue was purified with silica gel column chromatography to yield 17 mg of *N*-[1-(5-Methoxymethyl-[1,3,4]oxadiazole-2-carbonyl)-propyl]-4-oxo-2-benzylsulfonylmethyl-4-pyrrolidin-1-yl-butyramide; H^1 NMR($CDCl_3$): 8.2, 8(1H, d,d, NH, diastereomeric), 7.6-7.2(5H, m), 5.3-5.1(1H, m), 4.6(2H, s, OCH_2), 4.3-4.1(3H, m), 3.8-3.2(9H, m), 3-2.4(2H, m), 2.2-1.4(6H, m), 0.95(3H, t); MS:519.6(M-1), 521.6(M+1).

EXAMPLE 21

4-Morpholin-4-yl-4-oxo-2-benzylsulfonylmethyl-*N*-[1-(5-phenyl-[1,3,4]oxadiazole-2-carbonyl)-propyl]-butyramide

(Compound 77)



To a stirred mixture of 4-morpholin-4-yl-4-oxo-2-benzylsulfonylmethyl-butyric acid (177mg, 0.5mmol), 2-amino-1-(5-phenyl-[1,3,4]oxadiazol-2-yl)-1-butanol TFA salt (175mg), prepared as in reference 16, and HOBt (92mg, 0.6mmol) in $MeCl_2$ (5ml), was added EDC (144mg, 0.75mmol) and *N*-methylmorpholine (0.35ml) at room temperature. After stirring for 14 hours, the reaction mixture was extracted with ethyl acetate. The organic layer was washed with saturated $NaHCO_3$, brine, dried with $MgSO_4$ and concentrated to yield 308 mg of *N*-{1-[Hydroxy-(5-phenyl-[1,3,4]oxadiazol-2-yl)-methyl]-propyl}-4-morpholin-4-yl-4-oxo-2-benzylsulfonylmethyl-butyramide. Without further purification, the crude product was used for next reaction; MS: 569.6(M-1), 571.4(M+1).

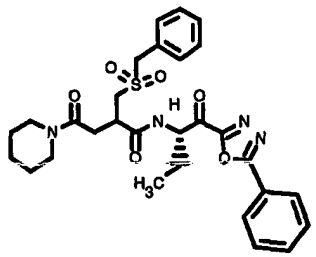
This amide was treated with Dess-Martin periodinane (371mg, 0.75mmol) at room temperature. After stirring for 1 hour, 5mls of saturated $Na_2S_2O_3$-$NaHCO_3$ were added. After a further 0.5 hours, the reaction mixture was extracted with ethyl acetate, washed with brine, dried with $MgSO_4$ and concentrated. The residue was purified with silica gel column chromatography to yield 224 mg of 4-morpholin-4-yl-4-oxo-2-benzylsulfonylmethyl-*N*-[1-(5-phenyl-[1,3,4]oxadiazole-2-carbonyl)-propyl]-butyramide; H^1 NMR(DMSO-d): 8.9, 8.84 (1H, d, d, NH, diastereomeric), 8.1-8(2H, m), 7.7-7.6(3H, m), 7.4-7.3(5H, m),5.1-4.9(1H, m), 4.5-4.3(2H, m), 3.6-3.3(11H, m), 3.12-3(1H, m), 2.65-2.5(1H, m) , 2-1.9(1H, m), 1.8-1.7(1H, m), 0.96(3H, t); MS: 567.6(M-1), 569.4(M+1).

EXAMPLE 22

4-Oxo-2-benzylsulfonylmethyl-*N*-[1-(5-phenyl-[1,3,4]oxadiazole-2-carbonyl)-propyl]-

4-piperidin-1-yl-butyramide

(Compound 78)



To a stirred mixture of 4-oxo-2-benzylsulfonylmethyl-4-piperidin-1-yl-butyric acid (177mg, 0.5mmol), 2-amino-1-(5-phenyl-[1,3,4]oxadiazol-2-yl)-1-butanol TFA salt (175mg) , prepared as in reference 16, and HOBt (92mg, 0.6mmol) in $MeCl_2$ (5ml), was added EDC (144mg, 0.75mmol) and *N*-methylmorpholine (0.35ml) at room temperature. After stirring for 14 hours, the reaction mixture was extracted with ethyl acetate. The organic layer was washed with saturated $NaHCO_3$, brine, dried with $MgSO_4$ and concentrated to yield 284 mg of *N*-{1-[Hydroxy-(5-phenyl-[1,3,4]oxadiazol-2-yl)-methyl]-propyl}-4-oxo-2-henylmethylsulfonylmethyl-4-piperidin-1-yl-butyramide. Without further purification, the crude product was used for next reaction; MS: 567.6(M-1), 569.6(M+1).

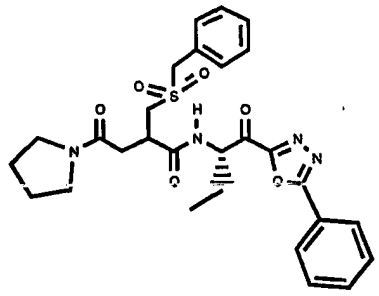
This amide was treated with Dess-Martin periodinane (371mg, 0.75mmol) at room temperature. After stirring for 1 hour, 5mls of saturated $Na_2S_2O_3$-$NaHCO_3$ were added. After a further 0.5 hours, the reaction mixture was extracted with ethyl acetate, washed with brine, dried with $MgSO_4$ and concentrated. The residue was purified with silica gel column chromatography to yield 237 mg of 4-oxo-2-benzylsulfonylmethyl-*N*-[1-(5-phenyl-[1,3,4]oxadiazole-2-carbonyl)-propyl]-4-piperidin-1-yl-butyramide; H^1 NMR (DMSO-d): 8.9, 8.84 (1H, d, d, NH, diastereomeric), 8.1-8(2H, m), 7.7-7.6(3H, m), 7.4-7.3(5H, m),5.1-4.9(1H, m), 4.5-4.3(2H, m), 3.4-3.1(7H, m), 3.12-3(1H, m), 2.65-2.5(1H, m) , 2-1.9(1H, m), 1.8-1.7(1H, m), 1.6-1.2(6H, m), 0.96(3H, t); MS: 565.4(M-1), 567.6(M+1).

EXAMPLE 23

4-Oxo-2-benzylsulfonylmethyl-*N*-[1-(5-phenyl-[1,3,4]oxadiazole-2-carbonyl)-

propyl]-4-pyrrolidin-1-yl-butyramide

(Compound 79)



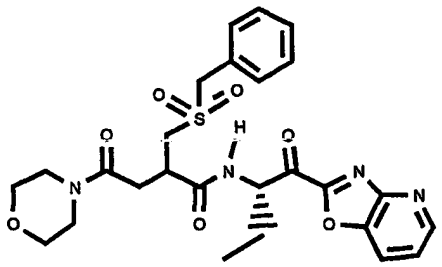
To a stirred mixture of 4-Oxo-2-benzylsulfonylmethyl-4-pyrrolidin-1-yl-butyric acid (170mg, 0.5mmol), 2-amino-1-(5-phenyl-[1,3,4]oxadiazol-2-yl)-1-butanol TFA salt (175mg), prepared as above, and HOBt (92mg, 0.6mmol) in $MeCl_2$ (5ml), was added EDC (144mg, 0.75mmol) and *N*-methylmorpholine (0.35ml) at room temperature. After stirring for 14 hours, the reaction mixture was extracted with ethyl acetate. The organic layer was washed with saturated $NaHCO_3$, brine, dried with $MgSO_4$ and concentrated to yield 280 mg of *N*-{1-[Hydroxy-(5-phenyl-[1,3,4]oxadiazol-2-yl)-methyl]-propyl}-4-oxo-2-henylmethylsulfonylmethyl-4-pyrrolidin-1-yl-butyramide. Without further purification, the crude product was used for next reaction; MS: 553.6(M-1), 555.4(M+1).

This amide was treated with Dess-Martin periodinane (371mg, 0.75mmol) at room temperature. After stirring for 1 hour, 5mls of saturated $Na_2S_2O_3$-$NaHCO_3$ were added. After a further 0.5 hours, the reaction mixture was extracted with ethyl acetate, washed with brine, dried with $MgSO_4$ and concentrated. The residue was purified with silica gel column chromatography to yield 200mg of 4-oxo-2-benzylsulfonylmethyl-*N*-[1-(5-phenyl-[1,3,4]oxadiazole-2-carbonyl)-propyl]-4-pyrrolidin-1-yl-butyramide; H^1 NMR (DMSO-d): 8.9, 8.84 (1H, d, d, NH, diastereomeric), 8.1-8(2H, m), 7.7-7.6(3H, m), 7.4-7.3(5H, m),5.1-4.9(1H, m), 4.5-4.3(2H, m), 3.4-3.1(7H, m), 3.12-3(1H, m), 2.65-2.5(1H, m), 2.1-1.6(6H, m), 0.96(3H, t); MS: 551.6(M-1), 553.6(M+1).

EXAMPLE 24

4-Morpholin-4-yl-*N*-[1-(oxazolo[4,5-b]pyridine-2-carbonyl)-propyl]-4-oxo-2-benzylsulfonylmethyl-butyramide

(Compound 80)



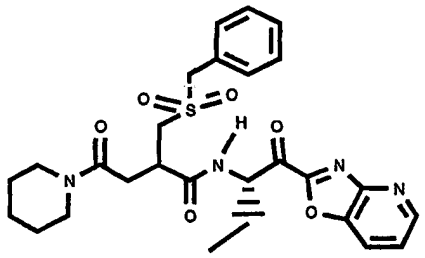
To a stirred mixture of 4-morpholin-4-yl-4-oxo-2-benzylsulfonylmethyl-butyric acid (177mg, 0.5mmol), 2-amino-1-(5-phenyl-[1,3,4]oxadiazol-2-yl)-1-butanol TFA salt (175mg), prepared as in reference 17, and HOBt (92mg, 0.6mmol) in $MeCl_2$ (5ml), was added EDC (144mg, 0.75mmol) and *N*-methylmorpholine (0.35ml) at room temperature. After stirring for 14 hours, the reaction mixture was extracted with ethyl acetate. The organic layer was washed with saturated $NaHCO_3$, brine, dried with $MgSO_4$ and concentrated to yield 308 mg of *N*-[1-(Hydroxy-oxazolo[4,5-*b*]pyridin-2-yl-methyl)-propyl]-4-morpholin-4-yl-4-oxo-2-benzylsulfonylmethyl-butyramide; MS: 543.6 (M-1), 545.6(M+1)

This amide was treated with Dess-Martin periodinane (371mg, 0.75mmol) at room temperature. After stirring for 1 hour, 5mls of saturated $Na_2S_2O_3$-$NaHCO_3$ were added. After a further 0.5 hours, the reaction mixture was extracted with ethyl acetate, washed with brine, dried with $MgSO_4$ and concentrated. The residue was purified with silica gel column chromatography to yield 224 mg of 4-morpholin-4-yl-*N*-[1-(oxazolo[4,5-b]pyridine-2-carbonyl)-propyl]-4-oxo-2-benzylsulfonylmethyl-butyramide; H^1 NMR (DMSO-d): 8.96, 8.85(1H, d,d, NH, diastereomeric), 8.75-8.7(1H, m), 8.42-8.3(1H, m), 7.7-7.6(1H, m), 7.4-7.3(5H, m), 5.15-5.04(1H, m), 4.5-4.3(2H, m), 3.6-3.2(11H, m), 3.15-3.0(1H, m), 2.7-2.5(1H, m), 2.1-1.9(1H, m), 1.8-1.7(1H, m), 0.98(3H, t); MS: 541.2(M-1), 543.2(M+1).

EXAMPLE 25

N-[1-(Oxazolo[4,5-b]pyridine-2-carbonyl)-propyl]-4-oxo-2-benzylsulfonyl-methyl-4-piperidin-1-yl-butyramide

(Compound 81)



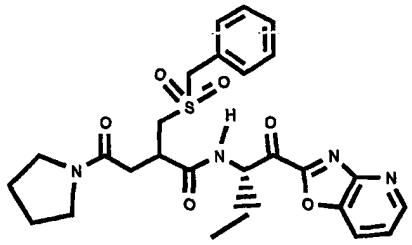
To a stirred mixture of 4-oxo-2-benzylsulfonylmethyl-4-piperidin-1-yl-butyric acid (177mg, 0.5mmol), 2-amino-1-(5-phenyl-[1,3,4]oxadiazol-2-yl)-1-butanol TFA salt (175mg) , prepared as in reference 17, and HOBt (92mg, 0.6mmol) in $MeCl_2$ (5ml), was added EDC (144mg, 0.75mmol) and N-methylmorpholine (0.35ml) at room temperature. After stirring for 14 hours, the reaction mixture was extracted with ethyl acetate. The organic layer was washed with saturated $NaHCO_3$, brine, dried with $MgSO_4$ and concentrated to yield 284 mg of *N*-[1-(hydroxy-oxazolo[4,5-*b*]pyridin-2-yl-methyl)-propyl]-4-oxo-2-henylmethylsulfonylmethyl-4-piperidin-1-yl-butyramide; MS: 541.6 (M-1), 543.4(M+1).

This amide was treated with Dess-Martin periodinane (371mg, 0.75mmol) at room temperature. After stirring for 1 hour, 5mls of saturated $Na_2S_2O_3$-$NaHCO_3$ were added. After a further 0.5 hours, the reaction mixture was extracted with ethyl acetate, washed with brine, dried with $MgSO_4$ and concentrated. The residue was purified with silica gel column chromatography to yield 237 mg of *N*-[1-(Oxazolo[4,5-b]pyridine-2-carbonyl)-propyl]-4-oxo-2-benzylsulfonyl-methyl-4-piperidin-1-yl-butyramide; H^1 NMR DMSO-d): 8.93, 8.83(1H, d,d, NH, diastereomeric), 8.75-8.72(1H, m), 8.4-8.37(1H, m), 7.7-7.6(1H, m), 7.4-7.3(5H, m), 5.15-5(1H, m), 4.5-4.3(2H, m), 3.45-3.2(9H, m), 3.1-3(1H, m), 2.67-2.5(1H, m), 2.1-1.9(1H, m), 1.84-1.7(1H, m), 1.6-1.5(2H, m), 1.5-1.3(4H, m), 0.98(3H, t); MS: 539.4(M-1), 541.2(M+1).

EXAMPLE 26

N-[1-(Oxazolo[4,5-b]pyridine-2-carbonyl)-propyl]-4-oxo-2-benzylsulfonyl-methyl-4-pyrrolidin-1-yl-butyramide

(Compound 82)



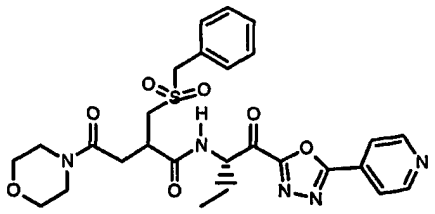
To a stirred mixture of 4-oxo-2-benzylsulfonylmethyl-4-pyrrolidin-1-yl-butyric acid (170mg, 0.5mmol), 2-amino-1-(5-phenyl-[1,3,4]oxadiazol-2-yl)-1-butanol TFA salt (175mg) , prepared as in reference 17, and HOBt (92mg, 0.6mmol) in $MeCl_2$ (5ml), was added EDC (144mg, 0.75mmol) and *N*-methylmorpholine (0.35ml) at room temperature. After stirring for 14 hours, the reaction mixture was extracted with ethyl acetate. The organic layer was washed with saturated $NaHCO_3$, brine, dried with $MgSO_4$ and concentrated to yield 280 mg of *N*-[1-(Hydroxy-oxazolo[4,5-*b*]pyridin-2-yl-methyl)-propyl]-4-oxo-2-henylmethylsulfonylmethyl-4-pyrrolidin-1-yl-butyramide. Without further purification, the crude product was used for next reaction; MS: 527.6(M-1), 529.4(M+1).

This amide was treated with Dess-Martin periodinane (371mg, 0.75mmol) at room temperature. After stirring for 1 hour, 5mls of saturated $Na_2S_2O_3$-$NaHCO_3$ were added. After a further 0.5 hours, the reaction mixture was extracted with ethyl acetate, washed with brine, dried with $MgSO_4$ and concentrated. The residue was purified with silica gel column chromatography to yield 200mg of *N*-[1-(Oxazolo[4,5-b]pyridine-2-carbonyl)-propyl]-4-oxo-2-benzylsulfonyl-methyl-4-pyrrolidin-1-yl-butyramide; H^1 NMR (DMSO-d): 8.96, 8.87(1H, d,d, NH, diastereomeric), 8.75-8.72(1H, m), 8.45-8.3(1H, m), 7.7-7.6(1H, m), 7.45-7.3(5H, m), 5.2-5(1H, m), 4.5-4.3(2H, m), 3.5-3.15(7H, m), 3.15-3(1H, m), 2.55-2.4(1H, m), 2.1-1.95(1H, m), 1.9-1.6(5H, m), 0.98(3H, t); MS: 525.2(M-1), 526.8(M+1).

EXAMPLE 27

4-Morpholin-4-yl-4-oxo-2-benzylsulfonylmethyl-*N*-[1-(5-pyridin-4-yl-[1,3,4]oxadiazole-2-carbonyl)-propyl]-butyramide

(Compound 83)



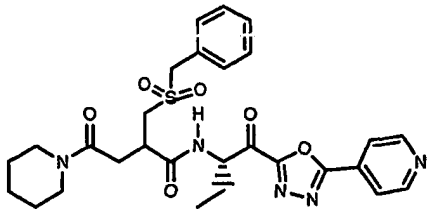
To a stirred mixture of 4-morpholin-4-yl-4-oxo-2-benzylsulfonylmethyl-butyric acid (106.5mg, 0.3mmol), 2-Amino-1-(5-pyridin-4-yl-[1,3,4]oxadiazol-2-yl)-butan-1-ol TFA salt (105mg), prepared as in reference 18, and HOBt (55mg, 0.36mmol) in $MeCl_2$ (5ml), was added EDC (86.4mg, 0.45mmol) and N-methylmorpholine (0.25ml) at room temperature. After stirring for 14 hours, the reaction mixture was extracted with ethyl acetate. The organic layer was washed with saturated $NaHCO_3$, brine, dried with $MgSO_4$ and concentrated, yield 176 mg of *N*-{1-[hydroxy-(5-pyridin-4-yl-[1,3,4]oxadiazol-2-yl)-methyl]-propyl}-4-oxo-2-benzylsulfonylmethyl-4-piperidin-1-yl-butyramide. MS: 568.4(M-1), 570(M+1)

This amide was treated with Dess-Martin periodinane (222.7mg, 0.45mmol) at room temperature. After stirring for 1 hour, 5mls of saturated $Na_2S_2O_3$-$NaHCO_3$ were added. After a further 0.5 hours, the reaction mixture was extracted with ethyl acetate, washed with brine, dried with $MgSO_4$ and concentrated. The residue was purified with silica gel column chromatography to yield 84mg of 4-morpholin-4-yl-4-oxo-2-benzylsulfonylmethyl-*N*-[1-(5-pyridin-4-yl-[1,3,4]oxadiazole-2-carbonyl)-propyl]-butyramide; H^1 NMR(DMSO-d): 8.95-8.85(3H, m), 8.1-8(2H, m), 7.44-7.3(5H, m), 5-4.9(1H, m), 4.5-4.3(2H, m), 3.4-3.(8H, m), 2.7-2.5(1H, m), 2.05-1.9(1H, m), 1.8-1.6(1H, m), 1.6-1.2(6H, m), 0.98(3H, t); MS: 566.6(M-1), 568.6(M+1).

EXAMPLE 28

4-Oxo-2-benzylsulfonylmethyl-4-piperidin-1-yl-*N*-[1-(5-pyridin-4-yl-[1,3,4]oxadiazole-2-carbonyl)-propyl]-butyramide

(Compound 84)



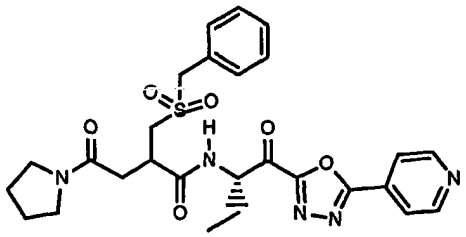
To a stirred mixture of 4-oxo-2-benzylsulfonylmethyl-4-piperidin-1-yl-butyric acid (105.9mg, 0.3mmol), 2-amino-1-(5-pyridin-4-yl-[1,3,4]oxadiazol-2-yl)-butan-1-ol TFA salt (105mg), prepared as in reference 18, and HOBt (55mg, 0.36mmol) in $MeCl_2$ (5ml), was added EDC (86.4mg, 0.45mmol) and *N*-methylmorpholine (0.25ml) at room temperature. After stirring for 14 hours, the reaction mixture was extracted with ethyl acetate. The organic layer was washed with saturated $NaHCO_3$, brine, dried with $MgSO_4$ and concentrated to yield 176mg of *N*-{1-[Hydroxy-(5-pyridin-4-yl-[1,3,4]oxadiazol-2-yl)-methyl]-propyl}-4-morpholin-4-yl-4-oxo-2-benzylsulfonyl-methyl-butyramide; MS: 570.2(M-1), 572(M+1).

This amide was treated with Dess-Martin periodinane (222.7mg, 0.45mmol) at room temperature. After stirring for 1 hour, 5mls of saturated $Na_2S_2O_3$-$NaHCO_3$ were added. After a further 0.5 hours, the reaction mixture was extracted with ethyl acetate, washed with brine, dried with $MgSO_4$ and concentrated. The residue was purified with silica gel column chromatography to yield 78 mg of 4-oxo-2-benzylsulfonyl-methyl-4-piperidin-1-yl-*N*-[1-(5-pyridin-4-yl-[1,3,4]oxadiazole-2-carbonyl)-propyl]-butyramide; H^1 NMR(DMSO-d): 9.0-8.85(3H, m), 8.1-8(2H, m), 7.44-7.3(5H, m), 5-4.9(1H, m), 4.5-4.3(2H, m), 3.6-3.2(11H, m), 3.15-3.05(1H, m), 2.7-2.5(1H, m), 2.05-1.9(1H, m), 1.8-1.7(1H, m), 0.96(3H, t); MS: 568.6(M-1), 570.6(M+1).

EXAMPLE 29

4-Oxo-2-benzylsulfonylmethyl-*N*-[1-(5-pyridin-4-yl-[1,3,4]oxadiazole-2-carbonyl)-propyl]-4-pyrrolidin-1-yl-butyramide

(Compound 85)



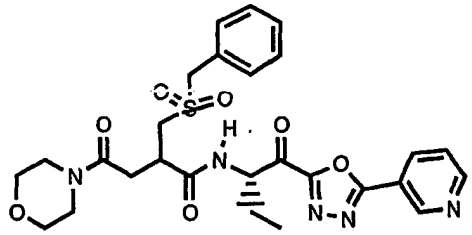
To a stirred mixture of 4-oxo-2-benzylsulfonylmethyl-4-pyrrolidin-1-yl-butyric acid (102mg, 0.3mmol), 2-amino-1-(5-pyridin-4-yl-[1,3,4]oxadiazol-2-yl)-butan-1-ol TFA salt (105mg), prepared as in reference 18, and HOBt (55mg, 0.36mmol) in $MeCl_2$ (5ml), was added EDC (86.4mg, 0.45mmol) and *N*-methylmorpholine (0.25ml) at room temperature. After stirring for 14 hours, the reaction mixture was extracted with ethyl acetate. The organic layer was washed with saturated $NaHCO_3$, brine, dried with $MgSO_4$ and concentrated to yield 210 mg of *N*-{1-[Hydroxy-(5-pyridin-4-yl-[1,3,4]oxadiazol-2-yl)-methyl]-propyl}-4-oxo-2-benzylsulfonylmethyl-4-pyrrolidin-1-yl-butyramide. MS: 554.2(M-1), 555.8(M+1).

This amide was treated with Dess-Martin periodinane (222.7mg, 0.45mmol) at room temperature. After stirring for 1 hour, 5mls of saturated $Na_2S_2O_3$-$NaHCO_3$ were added. After a further 0.5 hours, the reaction mixture was extracted with ethyl acetate, washed with brine, dried with $MgSO_4$ and concentrated. The residue was purified with silica gel column chromatography to yield 102 mg of 4-Oxo-2-benzylsulfonylmethyl-*N*-[1-(5-pyridin-4-yl-[1,3,4]oxadiazole-2-carbonyl)-propyl]-4-pyrrolidin-1-yl-butyramide; H^1 NMR (DMSO-d): 9.0-8.85(3H, m), 8.1-8(2H, m), 7.44-7.3(5H, m), 5.05-4.9(1H, m), 4.55-4.35(2H, m), 3.4-3.(8H, m), 2.6-2.4(1H, m), 2.05-1.9(1H, m), 1.9-1.6(5H, m), 0.96(3H, t); MS: 552.6(M-1), 554.6(M+1).

EXAMPLE 30

4-Morpholin-4-yl-4-oxo-2-benzylsulfonylmethyl-*N*-[1-(5-pyridin-3-yl-[1,3,4]oxadiazole-2-carbonyl)-propyl]-butyramide

(Compound 86)



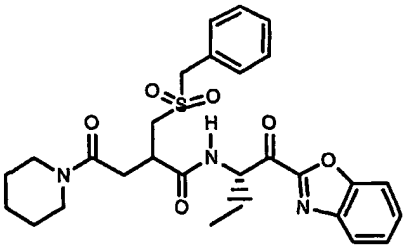
To a stirred mixture of 4-morpholin-4-yl-4-oxo-2-benzylsulfonylmethyl-butyric acid (177.7mg, 0.5mmol), 2-amino-1-(5-pyridin-3-yl-[1,3,4]oxadiazol-2-yl)-butan-1-ol TFA salt (180mg), prepared as in reference 19, and HOBt (92mg, 0.6mmol) in $MeCl_2$ (5ml), was added EDC (144mg, 0.75mmol) and *N*-methylmorpholine (0.25ml) at room temperature. After stirring for 14 hours, the reaction mixture was extracted with ethyl acetate. The organic layer was washed with saturated $NaHCO_3$, brine, dried with $MgSO_4$ and concentrated, yield 210 mg of *N*-{1-[Hydroxy-(5-pyridin-3-yl-[1,3,4]oxadiazol-2-yl)-methyl]-propyl}-4-morpholin-4-yl-4-oxo-2-benzylsulfonylmethyl-butyramide. Without further purification, the crude product was used for next reaction; MS: 570.4(M-1), 572.4(M+1).

This amide was treated with Dess-Martin periodinane (277mg, 0.56mmol) at room temperature. After stirring for 1 hour, 5mls of saturated $Na_2S_2O_3$-$NaHCO_3$ were added. After a further 0.5 hours, the reaction mixture was extracted with ethyl acetate, washed with brine, dried with $MgSO_4$ and concentrated. The residue was purified with silica gel column chromatography to yield 110 mg of 4-morpholin-4-yl-4-oxo-2-benzylsulfonylmethyl-*N*-[1-(5-pyridin-3-yl-[1,3,4]oxadiazole-2-carbonyl)-propyl]-butyramide; H^1 NMR(DMSO-d: 9.23(1H, s), 8.94, 8.88(1H, d,d, NH, diastereomeric), 8.87-8.8(1H, m), 8.46-8.4(1H, m), 7.7-7.6(1H, m), 7.4-7.25(5H, m), 5.05-4.9(1H, m), 4.55-4.3(2H, m), 3.6-3.15(11H, m), 3.14-3(1H, m), 2.7-2.5(1H, m), 2.05-1.9(1H, m), 1.8-1.65(1H, m), 0.98(3H, t); MS: 568.5(M-1), 570.3(M+1).

EXAMPLE 31

N-[1-(Benzooxazole-2-carbonyl)-propyl]-4-oxo-2-benzylsulfonylmethyl-4-piperidin-1-yl-butyramide

(Compound 87)



To a stirred mixture of 4-oxo-2-benzylsulfonylmethyl-4-piperidin-1-yl-butyric acid (141mg, 0.4mmol), 2-amino-1-benzooxazol-2-yl-butan-1-ol TFA salt. (129mg), prepared as in reference 20, and HOBt (74mg, 0.48mmol) in $MeCl_2$ (5ml), was added EDC (115mg, 0.6mmol) and N-methylmorpholine (0.25ml) at room temperature. After stirring for 14 hours, the reaction mixture was extracted with ethyl acetate. The organic layer was washed with saturated $NaHCO_3$, brine, dried with $MgSO_4$ and concentrated to yield 157mg of *N*-[1-(Benzooxazol-2-yl-hydroxy-methyl)-propyl]-4-oxo-2-enylmethylsulfonylmethyl-4-piperidin-1-yl-butyramide. Without further purification, the crude product was used for next reaction; MS: 540.4(M-1), 542.6(M+1).

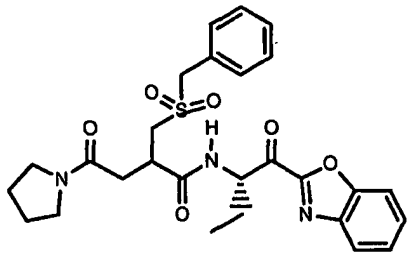
This amide was treated with Dess-Martin periodinane (215.3mg, 0.435mmol) at room temperature. After stirring for 1 hour, 5mls of saturated $Na_2S_2O_3$-$NaHCO_3$ were added. After a further 0.5 hours, the reaction mixture was extracted with ethyl acetate, washed with brine, dried with $MgSO_4$ and concentrated. The residue was purified with silica gel column chromatography to yield 103.3 mg of *N*-[1-(Benzooxazole-2-carbonyl)-propyl]-4-oxo-2-benzylsulfonylmethyl-4-piperidin-1-yl-butyramide; H^1 NMR(DMSO-d): 8.84, 8.76(1H, d,d, J=5.6Hz, J=6.4Hz, NH, diastereomeric), 8.02-7.96(1H, m), 7.92-7.86(1H, m), 7.68-7.62(1H, m), 7.58-7.52(1H, m), 7.44-7.32(5H, m), 5.24-5.12(1H, m), 4.52-4.38(2H, m), 3.5-3.22(7H, m), 3.12-3.02(1H, m), 2.64-2.52(1H, m), 2.04-1.94(1H, m),

1.8-1.68(1H, m), 1.6-1.48(2H, m), 1.48-1.32(4H, m), 0.98(3H, t, J=7.6Hz); MS: 540.4(M+1).

EXAMPLE 32

N-[1-(Benzooxazole-2-carbonyl)-propyl]-4-oxo-2-benzylsulfonylmethyl-4-pyrrolidin-1-yl-butyramide

(Compound 88)



To a stirred mixture of 4-oxo-2-benzylsulfonylmethyl-4-pyrrolidin-1-yl-butyric acid (135.6mg, 0.4mmol), 2-amino-1-benzooxazol-2-yl-butan-1-ol TFA salt (129mg), prepared as in reference 20, and HOBt (73.4mg, 0.48mmol) in $MeCl_2$ (5ml), was added EDC (115.2mg, 0.6mmol) and *N*-methylmorpholine (0.25ml) at room temperature. After stirring for 14 hours, the reaction mixture was extracted with ethyl acetate. The organic layer was washed with saturated $NaHCO_3$, brine, dried with $MgSO_4$ and concentrated to yield 260 mg of *N*-[1-(Benzooxazol-2-yl-hydroxy-methyl)-propyl]-4-oxo-2-henylmethylsulfonylmethyl-4-pyrrolidin-1-yl-butyramide. Without further purification, the crude product was used for next reaction; MS: 526.6(M-1), 528.6(M+1).

This amide was treated with Dess-Martin periodinane (215mg, 0.435mmol) at room temperature. After stirring for 1 hour, 5mls of saturated $Na_2S_2O_3$-$NaHCO_3$ were added. After a further 0.5 hours, the reaction mixture was extracted with ethyl acetate, washed with brine, dried with $MgSO_4$ and concentrated. The residue was purified with silica gel column chromatography to yield 199mg of *N*-[1-(Benzooxazole-2-carbonyl)-propyl]-4-oxo-2-benzylsulfonylmethyl-4-pyrrolidin-1-yl-butyramide; H^1 NMR(DMSO-d): 8.87, 8.79(1H, d,d, NH, J=6Hz, J=6.4Hz, diastereomeric), 8.04-7.96(1H, m), 7.92-7.86(1H, m),

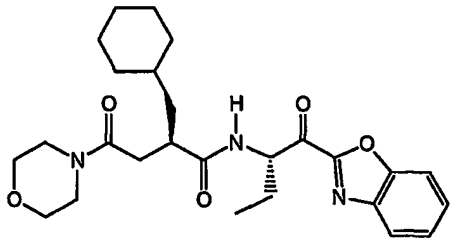
7.68-7.62(1H, m), 7.58-7.5(1H, m), 7.44-7.32(5H, m), 5.25-5.14(1H, m), 4.52-4.38(2H, m), 3.5-3.04(7H, m), 3.03-3.01(1H, m), 2.52-2.4(1H, m), 2.05-1.9(1H, m), 1.9-1.65(5H, m), 0.98(3H, m); MS: 526.3(M+1).

5

EXAMPLE 33

N-[1-(Benzooxazole-2-carbonyl)-propyl]-2-cyclohexylmethyl-4-morpholin-4-yl-4-oxo-butyramide

(Compound 89)



10

To a stirred mixture of 2-cyclohexylmethyl-4-morpholin-4-yl-4-oxo-butyric acid (84.9mg, 0.3mmol), 2-amino-1-benzooxazol-2-yl-butan-1-ol TFA salt(96.9mg), prepared as in reference 21, and HOBt (55.1mg, 0.36mmol) in $MeCl_2$ (5ml), was added EDC 15 (86.4mg, 0.45mmol) and *N*-methylmorpholine (0.25ml) at room temperature. After stirring for 14 hours, the reaction mixture was extracted with ethyl acetate. The organic layer was washed with saturated $NaHCO_3$, brine, dried with $MgSO_4$ and concentrated to yield 150 mg of *N*-[1-(benzooxazol-2-yl-hydroxy-methyl)-propyl]-2-cyclohexylmethyl-4-morpholin-4-yl-4-oxo-butyramide; MS: 470.5(M-1), 472.4(M+1).

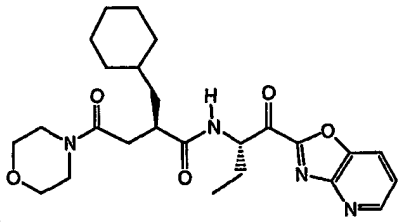
20 This amide was treated with Dess-Martin periodinane (237.6mg, 0.48mmol) at room temperature. After stirring for 1 hour, 5mls of saturated $Na_2S_2O_3$-$NaHCO_3$ were added. After a further 0.5 hours, the reaction mixture was extracted with ethyl acetate, washed with brine, dried with $MgSO_4$ and concentrated. The residue was purified with silica gel column chromatography to yield 76 mg of *N*-[1-(benzooxazole-2-carbonyl)-25 propyl]-2-cyclohexylmethyl-4-morpholin-4-yl-4-oxo-butyramide; H^1 NMR(DMSO-d): 8.49(1H, d, J=5.2Hz, NH), 7.96(1H, d, J=7.6Hz), 7.86(1H, d, J=8.4), 7.6(1H, m), 7.5(1H,

m), 5.14-5.04(1H, m), 3.6-3.25(8H, m), 2.9-2.75(1H, m), 2.5-2.4(1H, m), 2.25-2.15(1H, m), 2-1.8(1H, m), 1.8-1.7(2H, m), 1.7-1.6(1H, m), 1.6-1.4(5H, m), 1.35-1.2(1H, m), 1.2-1(4 H, m), 0.96(3H, t); MS: 468.6(M-1), 470.5(M+1), 492.3(M+Na).

EXAMPLE 34

2-Cyclohexylmethyl-4-morpholin-4-yl-*N*-[1-(oxazolo[4,5-b]pyridine-2-carbonyl)-propyl]-4-oxo-butyramide

(Compound 90)



To a stirred mixture of 2-cyclohexylmethyl-4-morpholin-4-yl-4-oxo-butyric acid (84.9mg, 0.3mmol), 2-amino-1-(5-phenyl-[1,3,4]oxadiazol-2-yl)-1-butanol TFA salt (97.5mg), prepared as in reference 21, and HOBt (55.1mg, 0.36mmol) in $MeCl_2$ (5ml), was added EDC (86.4mg, 0.45mmol) and *N*-methylmorpholine (0.25ml) at room temperature. After stirring for 14 hours, the reaction mixture was extracted with ethyl acetate. The organic layer was washed with saturated $NaHCO_3$, brine, dried with $MgSO_4$ and concentrated to yield 153mg of 2-cyclohexylmethyl-*N*-[1-(hydroxy-oxazolo[4,5-*b*]pyridin-2-yl-methyl)-propyl]-4-morpholin-4-yl-4-oxo-butyramide; MS: 471.6(M-1), 473.3(M+1).

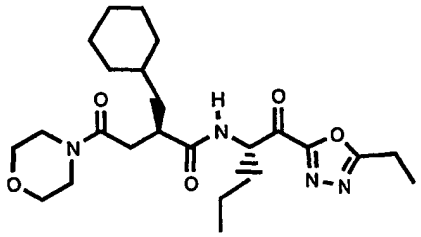
This amide was treated with Dess-Martin periodinane (237.6mg, 0.48mmol) at room temperature. After stirring for 1 hour, 5mls of saturated $Na_2S_2O_3$-$NaHCO_3$ were added. After a further 0.5 hours, the reaction mixture was extracted with ethyl acetate, washed with brine, dried with $MgSO_4$ and concentrated. The residue was purified with silica gel column chromatography to yield 95 mg of 2-cyclohexylmethyl-4-morpholin-4-yl-*N*-[1-(oxazolo[4,5-b]pyridine-2-carbonyl)-propyl]-4-oxo-butyramide; H^1 NMR(DMSO-d): 8.72-8.68(1H, m), 8.6(1H, d, J=5.2Hz, NH), 8.4-8.34(1H, m), 7.68-7.59(1H, m), 5.2-

4.96(1H, m), 3.5-3.45(8H, m), 2.58(1H, m), 2.5-2.4(1H, m), 2.45-2.15(1H, m), 2.05-1.9(1H, m), 1.85-1.65(2H, m), 1.6-1.4(5H, m), 1.3-1.2(1H, m), 1.25-1(4H, m), 0.97(3H, t); MS: 469.6(M-1), 471.4(M+1), 493.2(M+Na).

EXAMPLE 35

2-Cyclohexylmethyl-N-[1-(5-ethyl-[1,3,4]oxadiazole-2-carbonyl)-butyl]-4-morpholin-4-yl-4-oxo-butyramide

(Compound 91)



To a stirred mixture of 2-cyclohexylmethyl-4-morpholin-4-yl-4-oxo-butyric acid (84.9mg, 0.3mmol), 2-amino-1-(5-ethyl-1,3,4-oxadiazole-2-yl)-1-pentanol HCl salt (70.5mg), prepared as in reference 21, and HOBt (55.1mg, 0.36mmol) in $MeCl_2$ (5ml), was added EDC (86.4mg, 0.45mmol) and *N*-methylmorpholine (0.25ml) at room temperature. After stirring for 14 hours, the reaction mixture was extracted with ethyl acetate. The organic layer was washed with saturated $NaHCO_3$, brine, dried with $MgSO_4$ and concentrated to yield 142 mg of 2-cyclohexylmethyl-*N*-{1-[(5-ethyl-[1,3,4]oxadiazol-2-yl)-hydroxy-methyl]-butyl}-4-morpholin-4-yl-4-oxo-butyramide; MS: 463.5(M-1), 465.3(M+1).

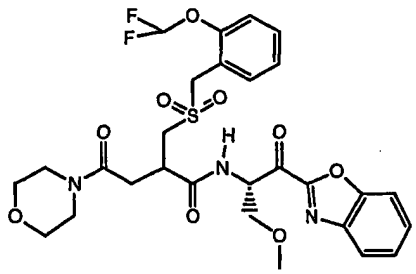
This amide was treated with Dess-Martin periodinane (239mg, 0.48mmol) at room temperature. After stirring for 1 hour, 5mls of saturated $Na_2S_2O_3$-$NaHCO_3$ were added. After a further 0.5 hours, the reaction mixture was extracted with ethyl acetate, washed with brine, dried with $MgSO_4$ and concentrated. The residue was purified with silica gel column chromatography to yield 65 mg of 2-cyclohexylmethyl-N-[1-(5-ethyl-[1,3,4]oxadiazole-2-carbonyl)-butyl]-4-morpholin-4-yl-4-oxo-butyramide; H^1 NMR

(DMSO-d): 8.6, 8.51(1H, dd, J=6.8Hz, J=5.6Hz, NH, diastereomeric), 4.98(-4.88(1H, m), 3.6-3.25(8H, m), 3-2.9(2H, q, J=7.6Hz), 2.9-2.75(1H, m), 2.5-2.4(1H, m), 2.3-2.1(1H, m), 1.9-1.7(2H, m), 1.7-1.4(7H, m), 1.4-1.2(2H, m), 1.28(3H, t), 1.2-1(6H, m), 0.88(3H, t); MS: 461.4(M-1), 463.4(M+1), 485.4(M+Na).

EXAMPLE 36

N-(2-Benzooxazol-2-yl-1-methoxymethyl-2-oxo-ethyl)-2-(2-difluoromethoxy-benzylsulfonylmethyl)-4-morpholin-4-yl-4-oxo-butyramide

(Compound 92)



To a stirred mixture of 2-(2-difluoromethoxy-benzylsulfonylmethyl)-4-morpholin-4-yl-4-oxo-butyric acid (210.5mg, 0.5mmol), 2-amino-1-benzooxazol-2-yl-3-methoxy-propan-1-ol (112.5mg), and HOBt (91.8mg, 0.6mmol) in $MeCl_2$ (5ml), was added EDC (144mg, 0.75mmol) and N-methylmorpholine (0.35ml) at room temperature. After stirring for 14 hours, the reaction mixture was extracted with ethyl acetate. The organic layer was washed with saturated $NaHCO_3$, brine, dried with $MgSO_4$ and concentrated to yield 301mg of *N*-(2-benzooxazol-2-yl-2-hydroxy-1-methoxymethyl-ethyl)-2-(2-difluoromethoxy-benzylsulfonylmethyl)-4-morpholin-4-yl-4-oxo-butyramide; MS: 624.5(M-1), 626.3(M+1).

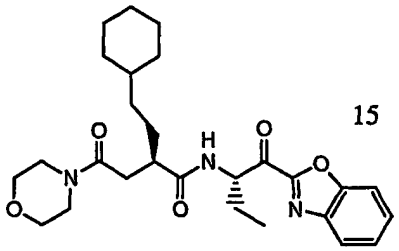
This amide(150mg, 0.24mmol) was treated with Dess-Martin periodinane (178mg, 0.36mmol) at room temperature. After stirring for 1 hour, 5ml of saturated $Na_2S_2O_3$-$NaHCO_3$ were added. After a further 0.5 hours, the reaction mixture was extracted with ethyl acetate, washed with brine, dried with $MgSO_4$ and concentrated. The residue was purified with silica gel column chromatography to yield 39 mg of *N*-(2-Benzooxazol-2-yl-

1-methoxymethyl-2-oxo-ethyl)-2-(2-difluoromethoxy-benzylsulfonylmethyl)-4-morpholin-4-yl-4-oxo-butyramide; H^1 NMR(DMSO-d): 8.97, 8.8(1H, dd, J=5.6Hz, J=5.6Hz, NH, diastereomeric), 8.02-7.94(1H, m), 7.9-7.84(1H, m), 7.66-7.58(1H, m), 7.55-7.38(3H, m), 7.3-7.18(2H, m), 7.1(1H, t, J=73.6Hz), 5.54-5.42(1H, m), 4.6-4.4(4H, m), 3.92-3.84(1H, m), 3.82-3.72(1H, m), 3.68-3.1(11H, m), 2.7-2.56(1H, m), 1.7-1.55(1H, m), 1.3-1(1H, m); MS: 622.4(M-1), 624.3(M+1), 646.3(M+Na).

EXAMPLE 37

N-[1-(Benzooxazole-2-carbonyl)-propyl]-2-(2-cyclohexyl-ethyl)-4-morpholin-4-yl-4-oxo-butyramide

(Compound 93)

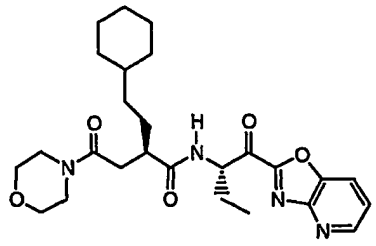


^{1}H NMR: (DMSO) 8.47 (d, J=6Hz, 1H), 7.96 (d, J=8.2Hz, 1H), 7.86 (d, J=8.2Hz, 1H), 7.59 (t, J=8.2Hz, 1H), 7.51 (t, J=8.2Hz, 1H), 5.09-5.03 (m, 1H), 3.56-3.27 (m, 8H), 2.72-2.64 (m, 1H), 2.54-2.46 (m, 1H), 2.21 (dd, J=15.8Hz, J=5.3Hz, 1H), 1.99-1.89 (m, 1H), 1.76-1.65 (m, 1H), 1.60-0.95 (m, 13H), 0.96 (t, J=7Hz, 3H), 0.72-0.60 (m, 2H). MS: $(M+H)^+$ 484.

EXAMPLE 38

2-(2-Cyclohexyl-ethyl)-4-morpholin-4-yl-*N*-[1-(oxazolo[4,5-b]pyridine-2-carbonyl)-propyl]-4-oxo-butyramide

(Compound 94)

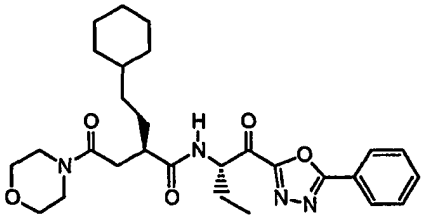


^{1}H NMR: (DMSO) 8.71-8.68 (m, 1H), 8.58 (d, J=4.7Hz, 1H), 8.36 (d, J=8.5Hz, 1H), 7.66-7.61 (m, 1H), 5.00-4.93 (m, 1H), 3.56-3.26 (m, 8H), 2.72-2.63 (m, 1H), 2.54-2.44 (m, 1H), 2.20 (dd, J=15.8Hz, J=5.3Hz, 1H), 2.02-1.92 (m, 1H), 1.78-1.67 (m, 1H), 1.60-0.95 (m, 13H), 0.97 (t, J=7Hz, 3H), 0.68-0.57 (m, 2H). MS: $(M+H)^+$ 485.

EXAMPLE 39

2-(2-Cyclohexyl-ethyl)-4-morpholin-4-yl-4-oxo-*N*-[1-(5-phenyl-[1,3,4]oxadiazole-2-carbonyl)-propyl]-butyramide

(Compound 95)

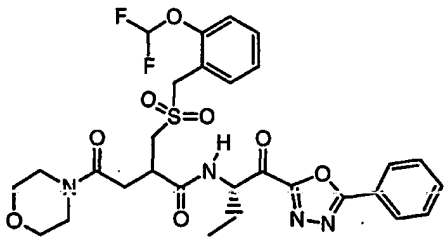


^{1}H NMR: (DMSO) 8.54 (d, J=4.7Hz, 1H), 8.10-8.04 (m, 2H), 7.70-7.58 (m, 3H), 4.91-4.85 (m, 1H), 3.55-3.22 (m, 8H), 2.70-2.62 (m, 1H), 2.56-2.45 (m, 1H), 2.22 (dd, J=15.5Hz, J=5Hz, 1H), 1.98-1.88 (m, 1H), 1.77-1.66 (m, 1H), 1.60-0.95 (m, 13H), 0.96 (t, J=7Hz, 3H), 0.75-0.60 (m, 2H). MS: $(M+H)^+$ 511.

EXAMPLE 40

2-(2-Difluoromethoxy-benzylsulfonylmethyl)-4-morpholin-4-yl-4-oxo-*N*-[1-(5-phenyl-[1,3,4]oxadiazole-2-carbonyl)-propyl]-butyramide

(Compound 96)

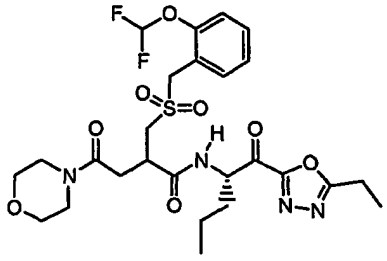


1:1 Mixture of diastereomers. ^{1}H NMR: (DMSO), 8.89 (d, J=5.6Hz), 8.82 (d, J=6Hz) 1H], 8.08-8.03 (m, 2H), 7.70-7.18 (m, 7H),, 7.11 (t, JH,F=74Hz), 7.08 (t, JH,F=74Hz) 1H], 5.01-4.90 (m, 1H), 4.56-4.43 (m, 2H), 3.56-3.13 (m, 10H), 2.68-2.40 (m, 3H), 2.00-1.90 (m, 1H), 1.78-1.68 (m, 1H), 0.96 (t, J=7Hz, 3H). MS: $(M+H)^+$ 635.

EXAMPLE 41

2-(2-Difluoromethoxy-benzylsulfonylmethyl)-*N*-[1-(5-ethyl-[1,3,4]oxadiazole-2-carbonyl)-butyl]-4-morpholin-4-yl-4-oxo-butyramide

(Compound 97)

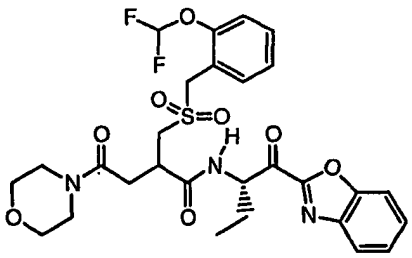


1:1 Mixture of diastereomers. ^{1}H NMR: (DMSO), 8.82 (d, J=5.5Hz), 8.77 (d, J=5Hz) 1H], 7.51-7.42 (m, 2H), 7.30-7.19 (m, 2H),, 7.11 (t, JH,F=74Hz), 7.10 (t, JH,F=74Hz) 1H], 5.02-4.92 (m, 1H), 4.56-4.43 (m, 2H), 3.58-3.26 (m, 10H), 3.20-3.12 (m, 1H), 2.98-2.89 (m, 2H), 2.68-2.44 (m, 2H), 1.86-1.76 (m, 1H), 1.69-1.58 (m, 1H), 1.46-1.20 (m, 5H), 0.88 (t, J=7Hz, 3H). MS: $(M+H)^+$ 601.

EXAMPLE 42

N-[1-(Benzooxazole-2-carbonyl)-propyl]-2-(2-difluoromethoxy-benzyl-sulfonylmethyl)-4-morpholin-4-yl-4-oxo-butyramide

(Compound 98)

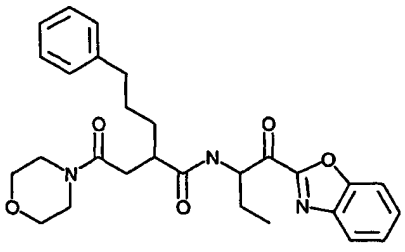


1:1 Mixture of diastereomers. ^{1}H NMR: (DMSO), 8.85 (d, J=5.3Hz), 8.76 (d, J=5.3Hz) 1H], 7.97 (t, J=6.5Hz, 1H), 7.89-7.84 (m, 1H), 7.64-7.18 (m, 6H),, 7.12 (t, JH,F=74Hz), 7.10 (t, JH,F=74Hz) 1H], 5.22-5.11 (m, 1H), 4.56-4.42 (m, 2H), 3.58-3.12 (m, 11H), 2.67-2.42 (m, 2H), 2.02-1.92 (m, 1H), 1.78-1.66 (m, 1H), 0.96 (t, J=7Hz, 3H). MS: $(M+H)^+$ 608.

EXAMPLE 43

2-(2-Morpholin-4-yl-2-oxo-ethyl)-5-phenyl-pentanoic acid, 1-(benzooxazole-2-carbonyl)-propyl]-amide

(Compound 99)



2-(2-Morpholin-4-yl-2-oxo-ethyl)-5-phenyl-pentanoic acid (83.7 mg, 0.274 mmol),

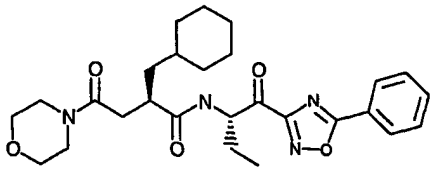
prepared as in reference 25, and HOBT (62.9 mg, 0.466 mmol) were added to a suspension of PS-bound N-Cyclohexylcarbodiimide (HL 200-400mesh cross linked with 2% DVB) from Novabiochem (322.3 mg, 0.548 mmol, 1.7 mmol/g loading) in methylene chloride (8 ml) and stirred at room temperature for 15 minutes. 2-Amino-1-benzooxazol-2-yl-butan-1-ol (56.5 mg. 0.274 mmol), prepared as in reference 20, was added and the reaction mixture stirred overnight at room temperature. Silicycle trisamine-3 (380.5 mg, 1.37 mmol, 3.6 mmol/g loading) was added and stirred for another 2 hours. The mixture was filtered and the filtrate evaporated under reduced pressure to give 2-(2-morpholin-4-yl-2-oxo-ethyl)-5-phenyl-pentanoic acid, 1-(benzooxazol-2-yl-hydroxy-methyl)-propyl]-amide as a yellow solid (128 mg).

To a solution of 2-(2-morpholin-4-yl-2-oxo-ethyl)-5-phenyl-pentanoic acid, 1-(benzooxazol-2-yl-hydroxy-methyl)-propyl]-amide (128 mg, 0.259 mmol) in methylene chloride (5 ml), Dess-Martin Periodinane (0.519 mmol, 220 mg) was added and stirred at room temperature for 90 minutes. The reaction mixture was washed with a solution of $Na_2S_2O_3$ in saturated $NaHCO_3$, dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by chromatography, eluting with a mixture of ethyl acetate and heptane, to give 2-(2-morpholin-4-yl-2-oxo-ethyl)-5-phenyl-pentanoic acid, 1-(benzooxazole-2-carbonyl)-propyl]-amide as a mixture of diastereoisomers (77 mg); ^1H NMR ($CDCl_3$) 7.90 (d, J=8Hz, 1H), 7.65 (d, J=8.2Hz, 1H), 7.55 (t, J=7.3Hz, 1H), 7.46 (t, J=7.2Hz, 1H), 7.4-7.1 (m, 5H),, 7.0 (d, J=7.4Hz), 6.76 (d, J=7.1Hz), 1H], 5.60 (m, 1H), 3.8-3.4 (m, 8H), 3.1-2.5 (m, 4H), 2.4-2.1 (m, 2H), 2.0-1.6 (m, 4H), 1.5 (m, 1H), 1.1 (m, 3H). MS : 492 (MH^+).

EXAMPLE 44

(R)-2-Cyclohexylmethyl-4-morpholin-4-yl-4-oxo-*N*-[(S)-1-(5-phenyl-1,2,4-oxadiazole-3-carbonyl)-propyl]-butyramide

(Compound 100)

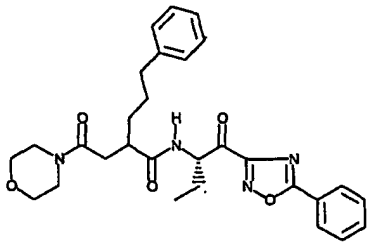


Similarly prepared according to the general procedure given for Example 43 but using (R)-2-cyclohexylmethyl-4-morpholin-4-yl-4-oxo-butyric acid, prepared as described in reference 21, and (S)-2-amino-1-(5-phenyl-[1,2,4]oxadiazol-3-yl)-butan-1-ol, prepared as in reference 26; MS: 519 (M+Na), LC-MS retention time 4.5 min; ^{1}H NMR ($CDCl_3$) 8.19 (d, J =7Hz, 2H), 7.65-7.51 (m. 3H), 6.64 (d, J=7Hz, 1H), 5.44-5.38 (m, 1H), 3.69-3.38 (m, 8H), 3.05-2.98 (m, 1H), 2.76 (dd, J=16Hz &10Hz, 1H), 2.26 (dd, J=16Hz & 3Hz, 1H), 2.10 (m, 1H), 1.80 (m, 1H), 1.75-1.59 (m, 6H), 1.28-1.13 (m, 5H), 1.03-0.98 (t, J = 7Hz, 3H), 0.92-0.81 (m, 2H).

EXAMPLE 45

2-(2-Morpholin-4-yl-2-oxo-ethyl)-5-phenyl-pentanoic acid, (S)-1-(5-phenyl-[1,2,4]oxadiazole-3-carbonyl)-propyl]-amide

(Compound 101)



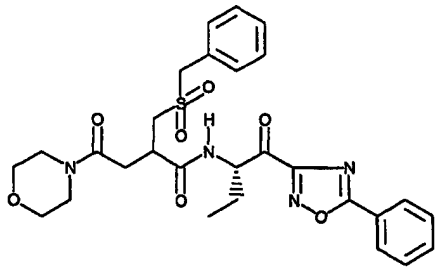
Similarly prepared according to the procedure for Example 43 but using 2-(2-morpholin-4-yl-2-oxo-ethyl)-5-phenyl-pentanoic acid and (S)-2-amino-1-(5-phenyl-[1,2,4]oxadiazol-3-yl)-butan-1-ol; MS : 541 (M+Na), LCMS retention time 4.44 and 4.53 min; ^{1}H NMR ($CDCl_3$) 8.18 (d, J= 7Hz, 2H), 7.69-7.51 (m, 3H), 7.27-7.10 (m, 5H), 6.99-6.7 (d, J=7Hz, 1H), 5.38 (m, 1H), 3.70-3.36 (m, 8H), 2.99-2.56 (m, 4H), 2.27 (m, 1H), 2.11

(m, 1H), 1.87-1.60 (m, 4H), 1.44 (m, 1H), 1.02-0.97(dt, J=7Hz, 3H).

EXAMPLE 46

4-Morpholin-4-yl-4-oxo-2-benzylsulfonylmethyl-*N*-[(S)-1-(5-phenyl-1,2,4-oxadiazole-3-carbonyl)-propyl]-butyramide

(Compound 102)

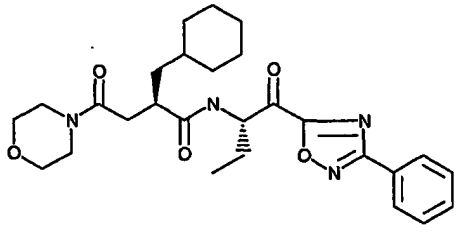


Similarly prepared according to the procedure for Example 43 but using 4-morpholin-4-yl-4-oxo-2-benzylsulfonylmethyl-butyric acid and (S)-2-amino-1-(5-phenyl-[1,2,4]oxadiazol-3-yl)-butan-1-ol; MS: 569 (MH^+), LCMS retention time 4.1 min; ^1H NMR ($CDCl_3$) 8.18 (d, J= 7.9Hz, 2H), 7.74-7.31 (m, 9H), 5.27 (m, 1H), 4.25 (m, 2H), 3.71-3.41 (m, 8H), 2.95 (m, 1H), 2.78-2.70 (m, 2H), 2.10 (m, 1H), 1.85 (m, 1H), 1.0 (m, 3H).

EXAMPLE 47

(R)-2-Cyclohexylmethyl-4-morpholin-4-yl-4-oxo-*N*-[(S)-1-(3-phenyl-1,2,4-oxadiazole-5-carbonyl)-propyl]-butyramide

(Compound 103)

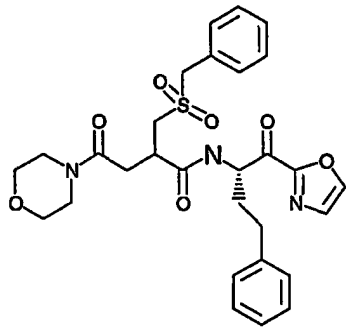


Similarly prepared according to the general procedure given for Example 43 above but using (R)-2-cyclohexylmethyl-4-morpholin-4-yl-4-oxo-butyric acid and (S)-2-amino-1-(3-phenyl-[1,2,4]oxadiazol-5-yl)-butan-1-ol; MS: 497 (MH^+).

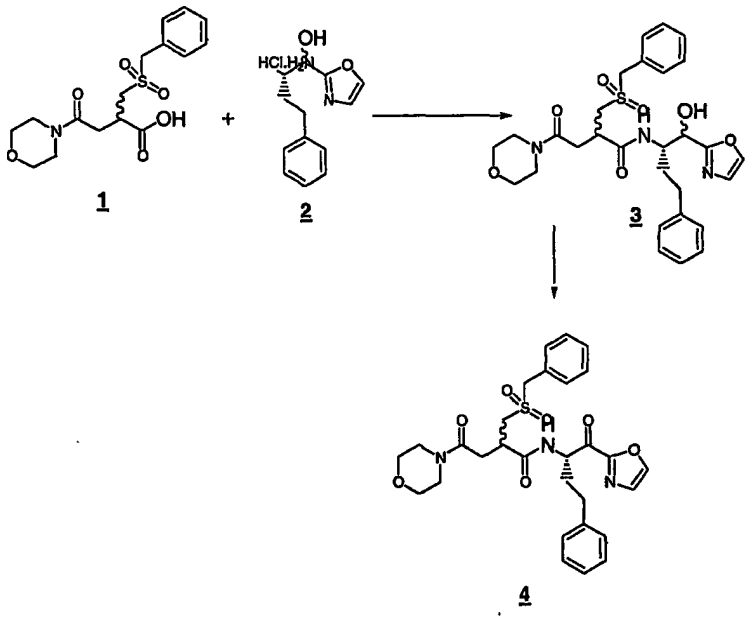
EXAMPLE 48

4-Morpholin-4-yl-*N*-[1-(oxazole-2-carbonyl)-3-phenyl-propyl]-4-oxo-2-benzylsulfonylmethyl-butyramide

(Compound 104)



Compound 104 was synthesized according to the following reaction protocol:

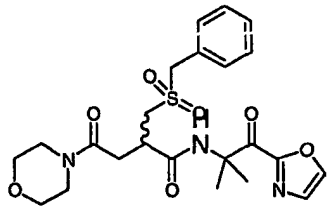


Compound 1 (0.1066g, 0.3mmol) and compound 2 (0.0806g, 0.3mmol) were mixed with EDC (0.0633g,0.33mmol), HOBT (0.0446g, 0.33mmol) and DIEA (0.2ml, 1.2mmol) in 3 ml of DMF which was stirred at room temperature overnight. The reaction was diluted with ethyl acetate and washed with cold 1N HCl, saturated sodium bicarbonate and brine. The organic layer was dried over magnesium sulfate, filtered and concentrated under reduced pressure. The crude product was purified using a 10g silica gel column eluting with 10% ethyl acetate/n-heptane to 80% ethyl acetate/n-heptane to give 79.4 mg (46%) of product 3. Compound 3 (73mg, 0.13mmol) was then dissolved in 1 ml of methylene chloride and Dess-Martin periodinane (15% in methylene chloride, 0.7358 g) was added and the reaction was allowed to at room temperature for 3 hours and excess Dess-Martin reagent was consumed by adding sodium thiosulfate in saturated sodium bicarbonate. The product was extracted with ethyl acetate and the organic layer was dried over magnesium sulfate, filtered and concentrated under reduced pressure. The product was purified using a 10g silica gel column eluting with 100% n-heptane to 30% n-heptane/ethyl acetate to yield 32.2 mg (44%) of the final compound 4; LCMS retention time 3:57 minutes, M+1(568.2).

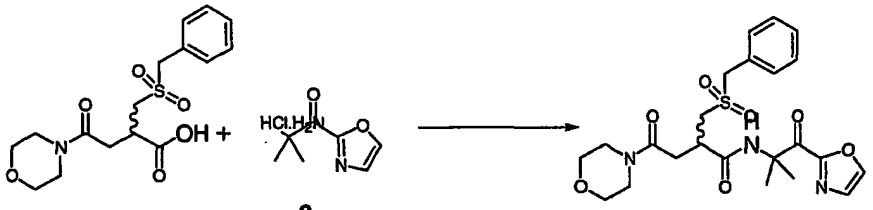
EXAMPLE 49

N-(1,1-Dimethyl-2-oxazol-2-yl-2-oxo-ethyl)-4-morpholin-4-yl-4-oxo-2-benzylsulfonylmethyl-butyramide

(Compound 105)



Compound 105 was synthesized according to the following reaction protocol:



1 2 3

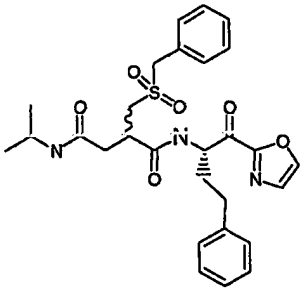
Compound 1 (0.1066g, 0.3mmol) and compound 2 (0.0572g, 0.3mmol) were mixed with EDC (0.0633g,0.33mmol), HOBT (0.0446g, 0.33mmol) and DIEA (0.2ml, 1.2mmol) in 3 ml of DMF which was stirred at room temperature overnight. The reaction was diluted with ethyl acetate and washed with cold 1N HCl, saturated sodium bicarbonate and brine. The organic layer was dried over magnesium sulfate, filtered and concentrated under reduced pressure. The crude product was purified using a 10g silica gel column eluting with 10% ethyl acetate/n-heptane to 80% ethyl acetate/n-heptane to give 15 mg (10%) of final product 3; LCMS retention time 3:10 minutes, M+1(492.2).

EXAMPLE 50

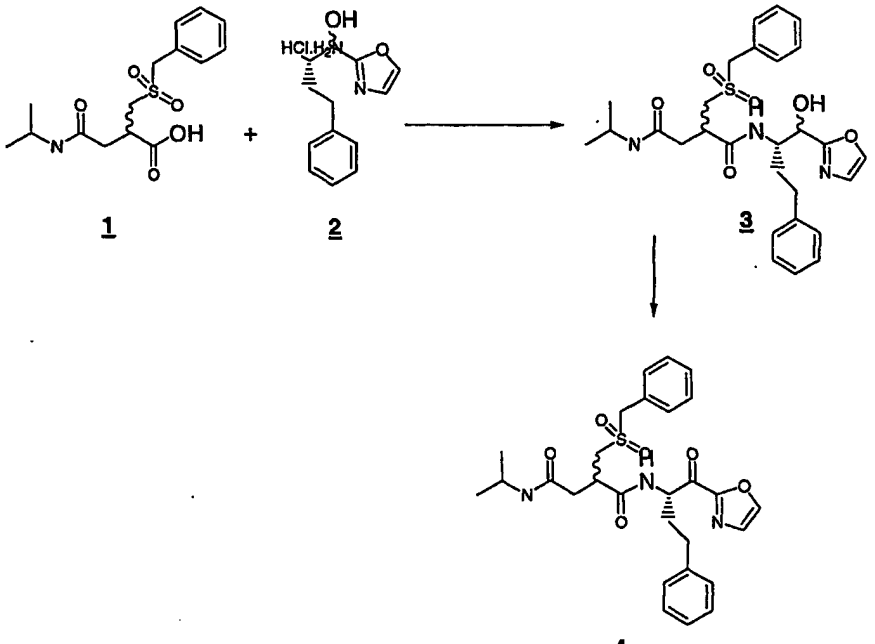
N-4-Isopropyl-*N*-1-[1-(oxazole-2-carbonyl)-3-phenyl-propyl]-2-benzylsulfonylmethyl-

succinamide

(Compound 106)



Compound 106 was synthesized according to the following reaction protocol:



1 2 3 4

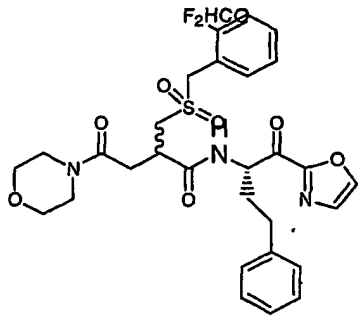
To a stirring suspension of N-Cyclohexylcarbodiimide, N'-methyl polystyrene resin (1.7 mmole/gram, 0.3529g, 0.6 mmol) in 10ml of methylene chloride was added the acid 1 (98.2 mg, 0.3mmol) and HOBT (69mg, 0.51mmol) which was allowed to stir for 15

minutes at room temperature. Compound 2 (80.6 mg, 0.3mmol) and DIEA (0.1ml, 0.5mmol) were added and the reaction was allowed to stir for 5 hours at room temperature. Then silicycle triamine™ (0.42g, 1.5mmol) was added and the reaction was stirred overnight at room temperature. The reaction was filtered and the solvent was removed under reduced pressure. The crude product 3 was used without further purification. Crude compound 3 was dissolved in methylene chloride and Dess-Martin reagent (15% in methylene chloride, 1.13g, 0.6mmol) was added and the reaction was allowed to stir at room temperature for 3 hours. The excess Dess-Martin reagent was consumed by adding sodium thiosulfate in saturated sodium bicarbonate. The product was extracted with ethyl acetate and washed with brine. The organic layer was dried over magnesium sulfate, filtered and concentrated under reduced pressure. The product was purified using HPLC to yield 15 mg of final compound 4; LCMS retention time 3:07 minutes, M+1(540.2).

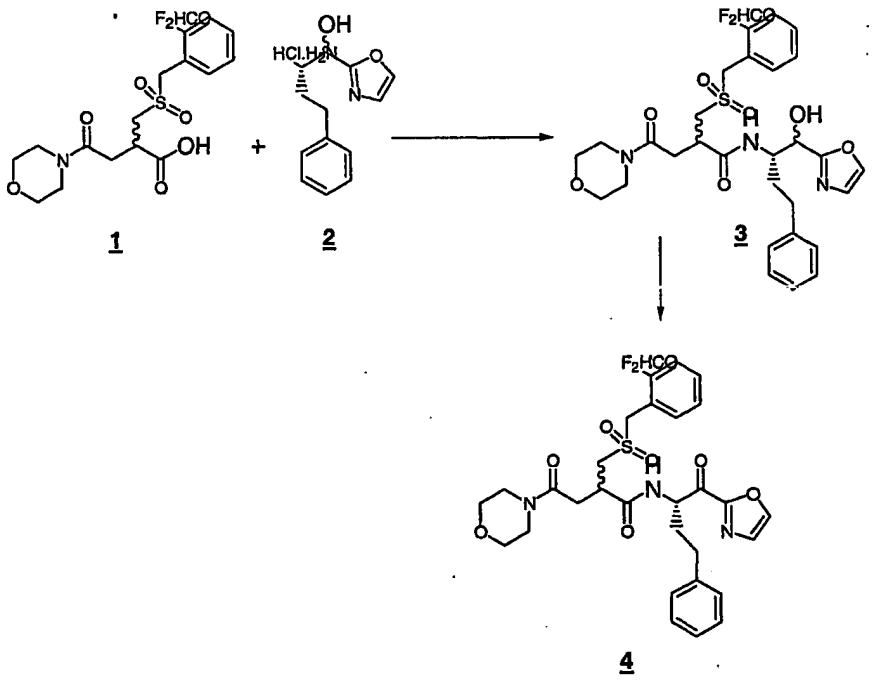
EXAMPLE 51

2-(2-Difluoromethoxy-benzylsulfonylmethyl)-4-morpholin-4-yl-*N*-[1-(oxazole-2-carbonyl)-3-phenyl-propyl]-4-oxo-butyramide

(Compound 107)



Compound 107 was synthesized according to the following reaction protocol:



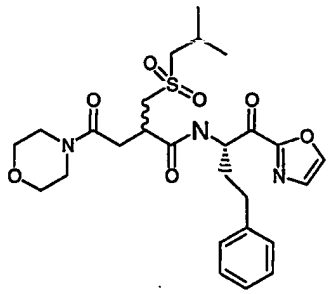
1 2 3 4

To a stirring suspension of *N*-Cyclohexylcarbodiimide, *N'*-methyl polystyrene resin (1.7 mmole/gram, 0.2353g, 0.4 mmol) in 10ml of methylene chloride was added the acid 1 (84.3 mg, 0.2mmol) and HOBT (45.9mg, 0.34mmol) which was allowed to stir for 15 minutes at room temperature. Compound 2 (53.75 mg, 0.2mmol) and DIEA (0.068ml, 0.4 mmol) were added and the reaction was allowed to stir for 5 hours at room temperature. Then silicycle triamine™ (0.28g, 1.0mmol) was added and the reaction was stirred overnight at room temperature. The reaction was filtered and the solvent was removed under reduced pressure. The crude product 3 was used without further purification. Crude compound 3 was dissolved in methylene chloride and Dess-Martin reagent (15% in methylene chloride, 1.13g, 0.6mmol) was added and the reaction was allowed to stir at room temperature for 3 hours. The excess Dess-Martin reagent was consumed by adding sodium thiosulfate in saturated sodium bicarbonate. The product was extracted with ethyl acetate and washed with brine. The organic layer was dried over magnesium sulfate, filtered and concentrated under reduced pressure. The product was purified using HPLC to yield 6 mg of final compound 4; LCMS retention time 3:09 minutes, M+1(634.4).

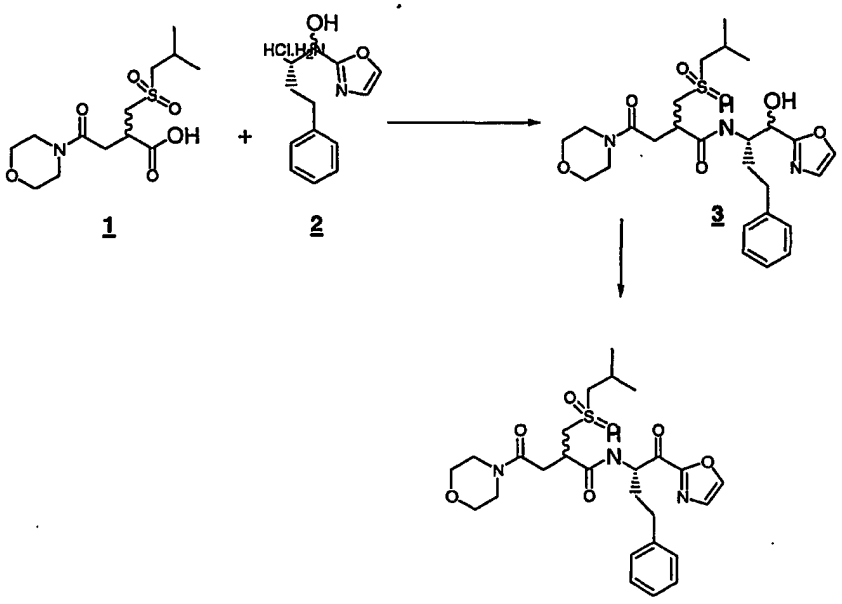
EXAMPLE 52

2-(2-Methyl-propane-1-sulfonylmethyl)-4-morpholin-4-yl-*N*-[1-(oxazole-2-carbonyl)-3-phenyl-propyl]-4-oxo-butyramide

(Compound 108)



Compound 108 was synthesized according to the following reaction protocol:



1 2 3 4

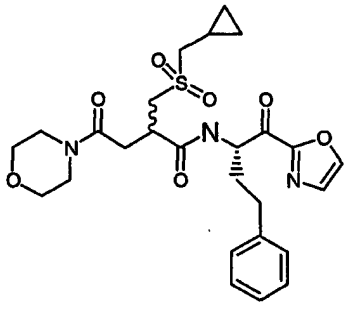
To a stirring suspension of *N*-Cyclohexylcarbodiimide, *N'*-methyl polystyrene resin (1.7 mmole/gram, 0.2353g, 0.4 mmol) in 10ml of methylene chloride was added the acid 1

(64.3 mg, 0.2mmol) and HOBT (45.9mg, 0.34mmol) which was allowed to stir for 15 minutes at room temperature. Compound 2 (53.75 mg, 0.2mmol) and DIEA (0.068ml, 0.4 mmol) were added and the reaction was allowed to stir for 5 hours at room temperature. Then silicycle triamine™ (0.28g, 1.0mmol) was added and the reaction was stirred overnight at room temperature. The reaction was filtered and the solvent was removed under reduced pressure. The crude product 3 was used without further purification. Crude compound 3 was dissolved in methylene chloride and Dess-Martin reagent (15% in methylene chloride, 1.13g, 0.6mmol) was added and the reaction was allowed to stir at room temperature for 3 hours. The excess Dess-Martin reagent was consumed by adding sodium thiosulfate in saturated sodium bicarbonate. The product was extracted with ethyl acetate and washed with brine. The organic layer was dried over magnesium sulfate, filtered and concentrated under reduced pressure. The product was purified using HPLC to yield 25.7 mg of final compound 4; LCMS retention time 2:89 minutes, M+1(534.4).

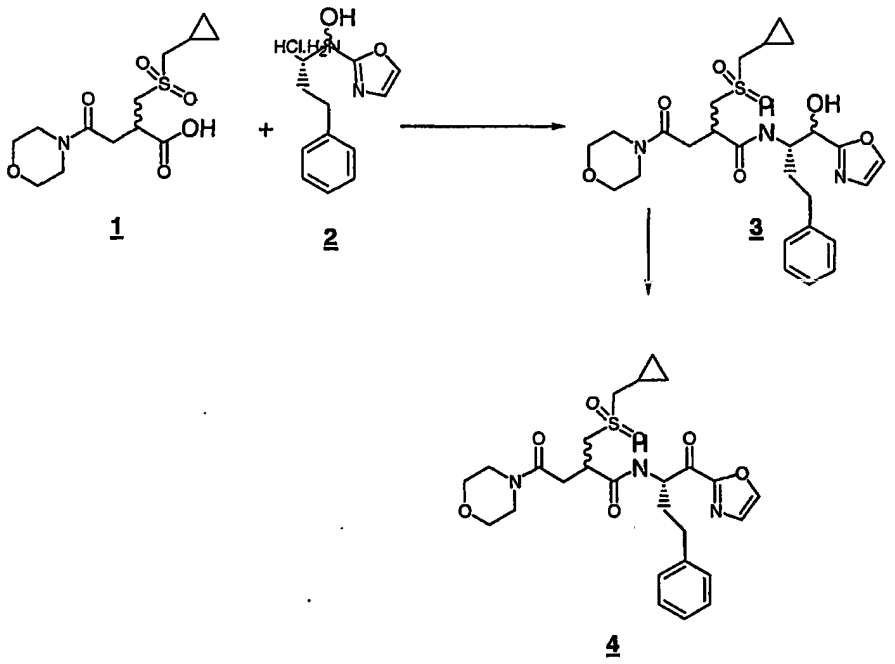
EXAMPLE 53

2-Cyclopropylmethylsulfonylmethyl-4-morpholin-4-yl-*N*-[1-(oxazole-2-carbonyl)-3-phenyl-propyl]-4-oxo-butyramide

(Compound 109)



Compound 109 was synthesized according to the following reaction protocol:



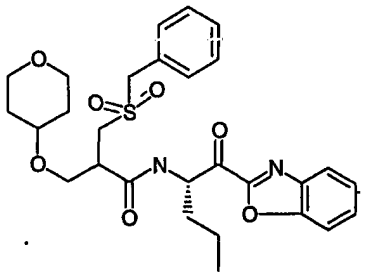
1 2 3 4

To a stirring suspension of *N*-Cyclohexylcarbodiimide, *N'*-methyl polystyrene resin (1.7 mmole/gram, 0.2353g, 0.4 mmol) in 10ml of methylene chloride was added the acid 1 (63.9 mg, 0.2mmol) and HOBT (45.9mg, 0.34mmol) which was allowed to stir for 15 minutes at room temperature. Compound 2 (53.75 mg, 0.2mmol) and DIEA (0.068ml, 0.4 mmol) were added and the reaction was allowed to stir for 5 hours at room temperature. Then silicycle triamine™ (0.28g, 1.0mmol) was added and the reaction was stirred overnight at room temperature. The reaction was filtered and the solvent was removed under reduced pressure. The crude product 3 was used without further purification. Crude compound 3 was dissolved in methylene chloride and Dess-Martin reagent (15% in methylene chloride, 1.13g, 0.6mmol) was added and the reaction was allowed to stir at room temperature for 3 hours. The excess Dess-Martin reagent was consumed by adding sodium thiosulfate in saturated sodium bicarbonate. The product was extracted with ethyl acetate and washed with brine. The organic layer was dried over magnesium sulfate, filtered and concentrated under reduced pressure. The product was purified using HPLC to yield 11.6 mg of final compound 4; LCMS retention time 2:77 minutes, M+1(532.4).

EXAMPLE 54

N-[1-(Benzooxazole-2-carbonyl)-butyl]-2-benzylsulfonyl-3-(tetrahydro-pyran-4-yloxymethyl)-propionamide

(Compound 110)



Diisopropylethylamine (0.184 ml, 1.05 mmol) was added to a mixture of 3-benzylsulfonyl-2-(tetrahydro-pyran-4-yloxymethyl)-propionic acid (362 mg, 1.05 mmol), prepared as in reference 27, and 2-amino-1-benzooxazol-2-yl-pentan-1-ol (238 mg, 1.05 mmol) and HATU (402 mg, 1.05 mmol) in DMF (10 ml) and stirred at room temperature overnight. Solvent was evaporated under reduced pressure, crude extract was taken up in ethyl acetate (30 ml) and washed with 1N HCl, saturated $NaHCO_3$ and brine. After drying over $MgSO_4$ the solvent was removed by rotary evaporation and the residue chromatographed on silica eluting with ethyl acetate/heptane mixture to give *N*-[(S)-1-(benzoxazol-2-yl-hydroxy-methyl)-butyl]-2-benzylsulfonylmethyl-3-(tetrahydro-pyran-4-yloxy)-propionamide (Yield: 258 mg); MS: 545 (M+1); LCMS retention time 3.71 and 3.76 minutes.

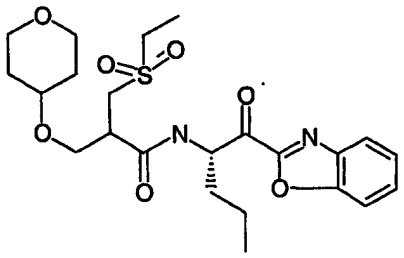
A solution of *N*-[(S)-1-(benzoxazol-2-yl-hydroxy-methyl)-butyl]-2-benzylsulfonylmethyl-3-(tetrahydro-pyran-4-yloxy)-propionamide (243 mg, 0.45 mmol) methylene chloride (8 ml) was treated with Dess-Martin periodinane (190 mg, 0.45 mmol) at room temperature for 2 hours. Washed with 0.26M solution of $Na_2S_2O_3$, $NaHCO_3$ and brine. After drying over $MgSO_4$ the solvent was removed by rotary evaporation and the residue chromatographed on silica eluting with ethyl acetate/heptane mixture to give *N*-[1-(benzooxazole-2-carbonyl)-butyl]-2-benzylsulfonyl-3-(tetrahydro-pyran-4-yloxymethyl)-propionamide as off white solid (Yield: 60 mg); MS: 543 (M+1); LCMS retention time 4.1

minutes.

EXAMPLE 55

N-[1-(Benzooxazole-2-carbonyl)-butyl]-3-ethanesulfonyl-2-(tetrahydro-pyran-4-yloxymethyl)-propionamide

(Compound 111)

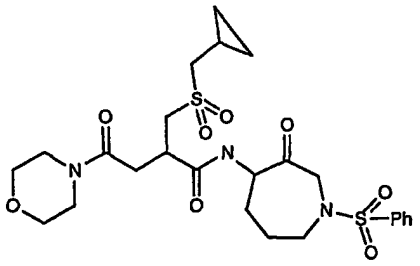


By following the method for Example 54 but substituting the required carboxylic acid with 3-ethylsulfonyl-2-(tetrahydro-pyran-4-yloxymethyl)-propionic acid, as prepared in reference 27b, *N*-[1-(benzooxazole-2-carbonyl)-butyl]-3-ethanesulfonyl-2-(tetrahydro-pyran-4-yloxymethyl)-propionamide was prepared. MS: 481 (M+1); LCMS retention time 3.7 minutes.

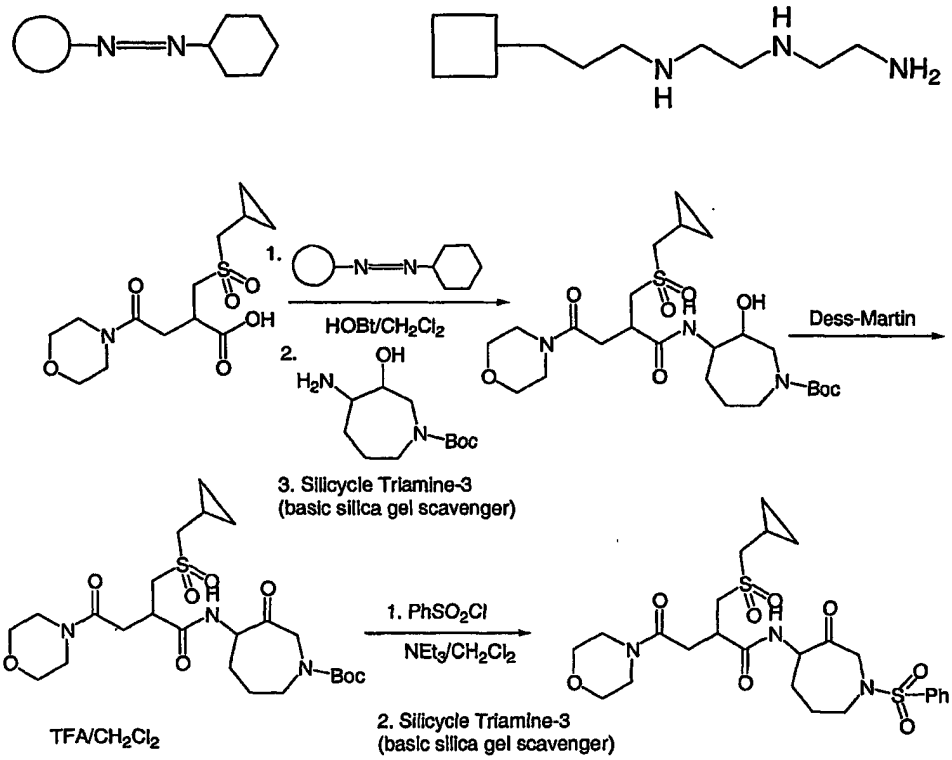
EXAMPLE 56

N-(1-Benzenesulfonyl-3-oxo-azepan-4-yl)-2-cyclopropylmethylsulfonylmethyl-4-morpholin-4-yl-4-oxo-butyramide

(Compound 112)



Compound 112 was prepared by the following protocol. The circle symbolizes the polystyrene backbone while the square symbolizes the silicium dioxide backbone:



1.16 mol-equivalents of the acid were dissolved in dichloromethyl. *N*-Cyclohexylcarbodiimide, *N'*-methylpolystyrene (2 mol-equivalents) and hydroxybenzotriazole (1.72 mol-equivalents) were added and the resulting reaction mixture stirred for 10 minutes. 4-Amino-3-hydroxy-azepane-1-carboxylic acid tert-butyl ester (1

mol-equivalent) was added and stirring continued for 21 hours. Silicycle-Triamine-3™ was added and the resulting mixture stirred for six hours. The mixture was filtered under suction and the filtrate concentrated under vacuum.

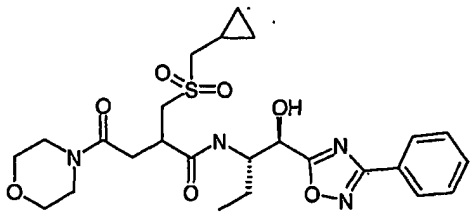
The alcohol was dissolved in dichloromethyl and 2 mol-equivalents of Dess-Martin periodinane were added to the solution. The reaction mixture was stirred for one hour. Equal volumes of saturated sodium thiosulfate solution and sat sodium bicarbonate solution were added and the phases separated. The aqueous phase was extracted three times with dichloromethyl. The combined organic phases were washed with saturated sodium bicarbonate solution and saturated sodium chloride solution. The solution was dried with magnesium sulfate and the solvents evaporated.

The azepanone-1-carboxylic acid tert-butyl ester was dissolved in a dichloromethyl solution (20vol-%) of trifluoroacetic acid. After stirring for one hour dichloromethyl was removed under reduced pressure and trifluoroacetic acid under high vacuum. The solid residue was re-dissolved in dichloromethyl and five mol-equivalent of triethylamine were added. 1.2 mol-equivalent of benzenesulfonyl chloride were added and the reaction mixture stirred for four hours. 12 mol-equivalents of Silicycle Triamine™ were added and stirring continued for two hours. The mixture was filtered under suction and the dichloromethyl evaporated under reduced pressure. The crude product was purified via preparative HPLC yielding *N*-(1-benzenesulfonyl-3-oxo-azepan-4-yl)-2-cyclopropylmethylsulfonylmethyl-4-morpholin-4-yl-4-oxo-butyramide as an off-white solid; LC/MS retention time 2.61 minutes, m/z=570 (M+H).

The following examples were prepared according to methods described in Example 56:

2-Cyclopropylmethylsulfonylmethyl-N-{(S)-1-[(R)-hydroxy-(3-phenyl-1,2,4-oxadiazol-5-yl)-methyl]-propyl}-4-morpholin-4-yl-4-oxo-butyramide

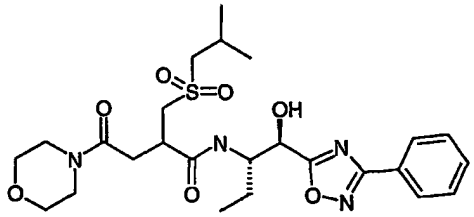
(Compound 122)



Tan solid; LC/MS retention time 3.456 minutes (TIC), m/z=557 (M+Na).

N-{(S)-1-[(R)-hydroxy-(3-phenyl-1,2,4-oxadiazol-5-yl)-methyl]-propyl}-2-(2-methyl-propane-1-sulfonylmethyl)-4-morpholin-4-yl-4-oxo-butyramide

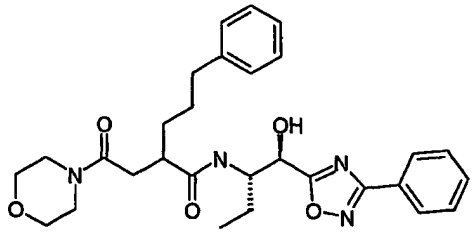
(Compound 123)



Tan solid; LC/MS retention time 3.594 minutes (TIC), m/z=559 (M+Na).

2-(2-Morpholin-4-yl-2-oxo-ethyl)-5-phenyl-pentanoic acid {(S)-1-[(R)-hydroxy-(3-phenyl-1,2,4-oxadiazol-5-yl)-methyl]-propyl}-amide

(Compound 124)

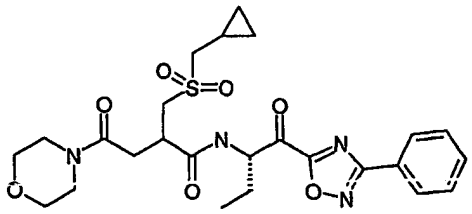


Tan solid; LC/MS retention time 3.379 minutes (TIC), m/z=521 (M+H).

2-Cyclopropylmethylsulfonylmethyl-4-morpholin-4-yl-4-oxo-N-[(S)-1-(3-phenyl-1,2,4-

oxadiazole-5-carbonyl)-propyl]-butyramide

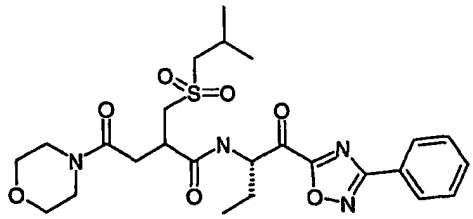
(Compound 125)



Tan solid; LC/MS retention time 2.976 minutes (TIC), m/z=533 (M+H).

2-(2-methyl-propane-1-sulfonylmethyl)-4-morpholin-4-yl-4-oxo-N-[(S)-1-(3-phenyl-1,2,4-oxadiazole-5-carbonyl)-propyl]-butyramide

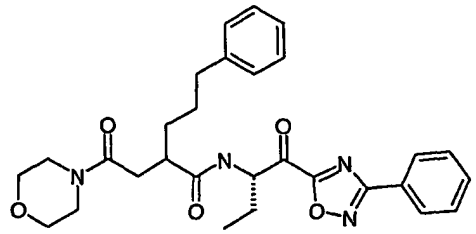
(Compound 126)



Tan solid; LC/MS retention time 3.433 minutes (TIC), m/z=535 (M+H).

2-(2-Morpholin-4-yl-2-oxo-ethyl)-5-phenyl-pentanoic acid, (S)-1-(3-phenyl-1,2,4-oxadiazole-5-carbonyl)-propyl}-amide

(Compound 127)

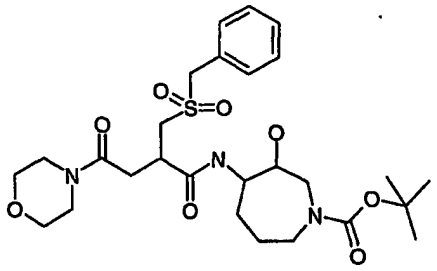


Tan solid; LC/MS retention time 3.762 minutes (TIC), m/z=519 (M+H).

EXAMPLE 57

3-Hydroxy-4-(4-morpholin-4-yl-4-oxo-2-benzylsulfonylmethyl-butyrylamino)-azepane-1-carboxylic acid tert-butyl ester

(Compound 113)

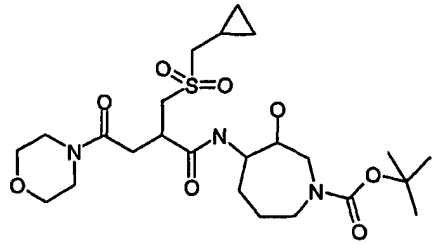


Tan solid prepared according to example 56; LC/MS retention time 2.985 minutes (TIC), m/z=568 (M+H) and 590 (M+Na).

EXAMPLE 58

4-(2-Cyclopropylmethylsulfonylmethyl-4-morpholin-4-yl-4-oxo-butyrylamino)-3-hydroxy-azepane-1-carboxylic acid tert-butyl ester

(Compound 114)

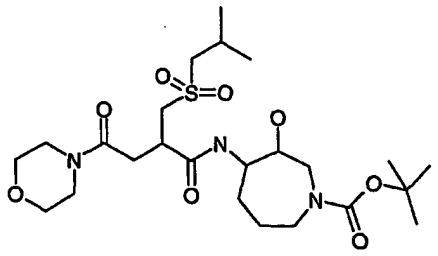


Tan solid prepared according example 56; LC/MS retention time 2.786 minutes (TIC), m/z=532 (M+H) and 554 (M+Na).

EXAMPLE 59

3-Hydroxy-4-[2-(2-methyl-propane-1-sulfonylmethyl)-4-morpholin-4-yl-4-oxo-butyrylamino]-azepane-1-carboxylic acid tert-butyl ester

(Compound 115)

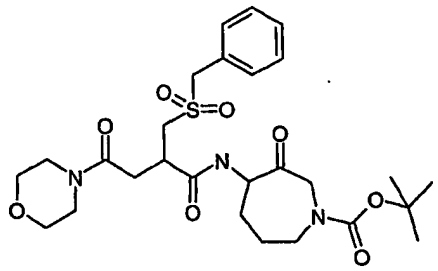


Tan solid prepared according example 56; LC/MS retention time 2.903 minutes (TIC), m/z=534 (M+H).

EXAMPLE 60

4-(4-Morpholin-4-yl-4-oxo-2-benzylsulfonylmethyl-butyrylamino)-3-oxo-azepane-1-carboxylic acid tert-butyl ester

(Compound 116)

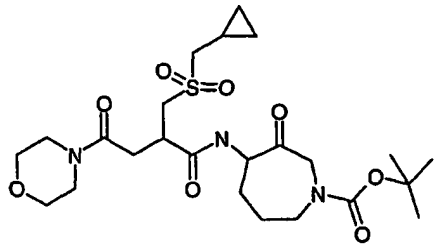


Tan solid prepared according example 56; LC/MS retention time 3.163 minutes (TIC), m/z=566 (M+H).

EXAMPLE 61

4-(2-Cyclopropylmethylsulfonylmethyl-4-morpholin-4-yl-4-oxo-butyrylamino)-3-oxo-azepane-1-carboxylic acid tert-butyl ester

(Compound 117)

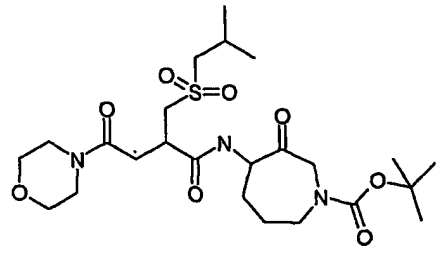


Tan solid prepared according to example 56; LC/MS retention time 2.965 minutes (TIC), m/z=530 (M+H).

EXAMPLE 62

4-[2-(2-Methyl-propane-1-sulfonylmethyl)-4-morpholin-4-yl-4-oxo-butyrylamino]-3-oxo-azepane-1-carboxylic acid tert-butyl ester

(Compound 118)

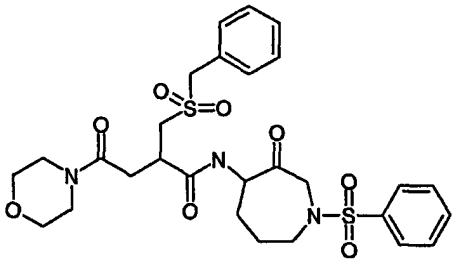


Tan solid prepared according to example 56; LC/MS retention time 3.083 minutes (TIC), m/z=532 (M+H).

EXAMPLE 63

N-(1-Benzenesulfonyl-3-oxo-azepan-4-yl)-4-morpholin-4-yl-4-oxo-2-benzylsulfonylmethyl-butyramide

(Compound 119)

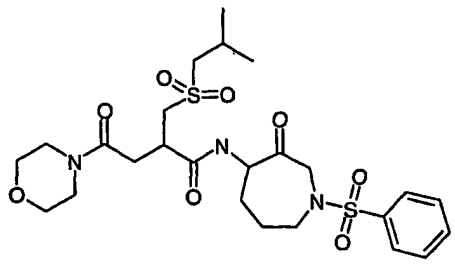


Off-white solid prepared according example 56; LC/MS retention time 2.83 minutes (TIC), m/z=606 (M+H).

EXAMPLE 64

N-(1-Benzenesulfonyl-3-oxo-azepan-4-yl)-2-(2-methyl-propane-1-sulfonylmethyl)-4-morpholin-4-yl-4-oxo-butyramide

(Compound 120)



Off-white solid prepared according example 56; *LC/MS* retention time 2.72 minutes (TIC), m/z=572 (M+H).

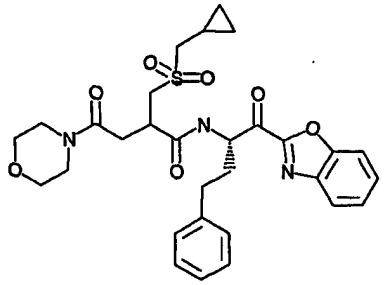
5

EXAMPLE 65

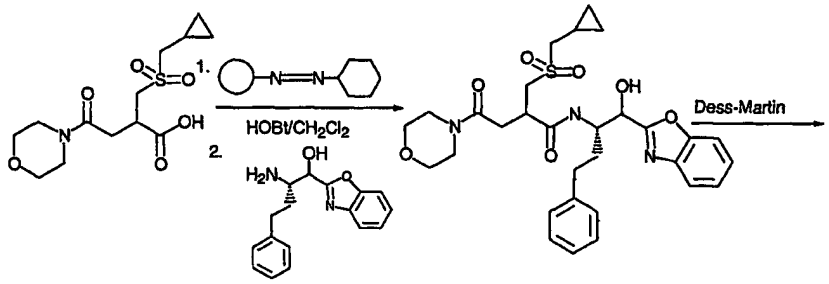
N-[(1S)-1-(Benzooxazol-2-yl-hydroxy-methyl)-3-phenyl-propyl]-2-cyclopropylmethylsulfonylmethyl-4-morpholin-4-yl-4-oxo-butyramide

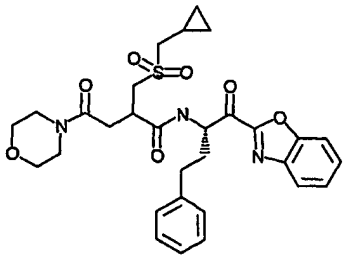
(Compound 121)

10



Compound 121 was prepared according to the following reaction scheme:



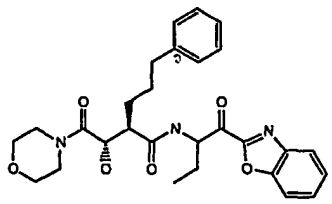


0.25mmol (1.16 mol-equivalent) of 2-cyclopropylmethylsulfonylmethyl-4-morpholin-4-yl-4-oxo-butyric acid was dissolved in 10ml dichloromethyl. 252mg, 0.43mmol *N*-cyclohexylcarbodiimide, *N'*-methylpolystyrene (2 mol-equivalents) and 50mg, 0.37mmol hydroxybenzotriazole (1.72 mol-equivalents) were added and the resulting reaction mixture stirred for 10 minutes. 61mg, 0.215mmol 2-amino-1-benzooxazol-2-yl-4-phenyl-butan-1-ol (1 mol-equivalents) was added and stirring continued for 21 hours. 510mg, 2.15mmol Silicycle-Triamine-3™ was added and the resulting mixture stirred for 6 hours. The mixture was filtered under suction and the filtrate concentrated under vacuum yielding 83mg, 0.142mmol (66%) of *N*-[(1S)-1-(Benzooxazol-2-yl-hydroxy-methyl)-3-phenyl-propyl]-2-cyclopropylmethylsulfonyl-0methyl-4-morpholin-4-yl-4-oxo-butyramide as a tan solid; LC/MS retention time 3.256min (TIC), m/z=584 (M+H).

EXAMPLE 66

(R)-2-((S)-1-Hydroxy-2-morpholin-4-yl-2-oxo-ethyl)-5-phenyl-pentanoic acid, 1-(benzoxazole-2-carbonyl)-propyl]-amide

(Compound 128)



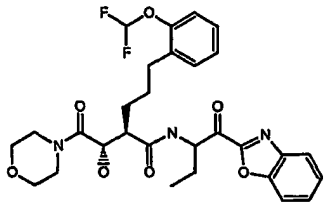
PyBOP (126 mg, 0.24 mmol), DIPEA (0.096 ml, 0.55mmol) and 2-Amino-1-benzooxazol-2-yl-butan-1-one hydrochloride (53 mg, 0.22 mmol) were added to a solution of (R)-2-((S)-1-Hydroxy-2-morpholin-4-yl-2-oxo-ethyl)-5-phenyl-pentanoic acid (70.7 mg, 0.22 mmol) in dry methylene chloride (5 ml) and the reaction mixture was stirred overnight at room temperature. The reaction was concentrated under reduced pressure, the residue

dissolved in ethyl acetate and washed with water. Organic extract was dried over $MgSO_4$ and evaporated under reduced pressure. Column chromatography on silica eluting with a mixture of ethyl acetate and heptane gave the title compound as white solid (38 mg); ^1H NMR ($CDCl_3$) δ 1.02 (t, J=7.4Hz, 3H), 1.97-1.62 (m, 5H), 2.21-2.15 (m, 1H), 2.74-2.59 (m, 3H), 3.65-3.49 (m, 8H), 4.41 (m, 1H), 4.70 (m, 1H), 5.62 (m, 1H), 6.93 (d, J=7.1Hz) 6.68 (d, J=7.1Hz, 1H), 7.33-7.13 (m, 5H), 7.49 (t, J=8Hz, 1H), 7.57 (t, J=8Hz, 1H), 7.66 (d, J=5.9, 1H), 7.92 (d, J=8Hz, 1H); MS: 508(MH^+); LC/MS retention time was 3.05 minutes.

EXAMPLE 67

(R)-5-(2-Difluoromethoxy-phenyl)-2-((S)-1-hydroxy-2-morpholin-4-yl-2-oxo-ethyl)-pentanoic acid, 1-(benzoxazole-2-carbonyl)-propyl]-amide

(Compound 129)



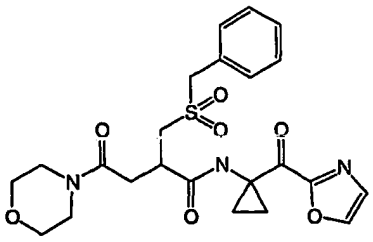
Similarly prepared according to the procedure in Example 66 but using (R)-5-(2-difluoromethoxy-phenyl)-2-((S)-1-hydroxy-2-morpholin-4-yl-2-oxo-ethyl)-pentanoic acid as the acidic component; ^1H NMR ($CDCl_3$) δ 1.06 (t, J=7.5Hz, 3H), 1.97-1.63 (m, 5H), 2.23-2.14 (m, 1H), 2.79-2.68 (m, 3H), 3.75-3.50 (m, 8H), 4.42 (m, 1H), 4.81-4.62 (m, 1H), 5.61 (m, 1H), 6.53 (t, J=74Hz, 1H), 6.73 (d, J=7.1Hz), 6.98 (d, J=7.1Hz, 1H), 7.24-7.06 (m, 4H), 7.59-7.49 (m, 2H), 7.69-7.64 (m, 1H), 7.91 (d, J=7.9Hz, 1H); MS: 574(MH^+).

EXAMPLE 68

4-Morpholin-4-yl-N-[1-(oxazole-2-carbonyl)-cyclopropyl]-4-oxo-2-benzylsulfonyl

methyl –butyramide

(Compound 130)



Similarly prepared according to the procedure in Example 66 but using 4-morpholin-4-yl-4-oxo-2-benzylsulfonylmethyl-butyric acid as the acidic component and (1-Amino-cyclopropyl)-oxazol-2-yl-methanone hydrochloride as the basic component; MS: 490 (MH^+); LC/MS, retention time 2.44 minutes.

EXAMPLE 69

Cathepsin S Assay

Solutions of test compounds in varying concentrations were prepared in 10 μL of dimethyl sulfoxide (DMSO) and then diluted into assay buffer (40 μL, comprising: MES, 50 mM (pH 6.5); EDTA, 2.5 mM; and NaCl, 100 mM). Human cathepsin S (0.158 pMoles in 25 μL of assay buffer) was added to the dilutions. The assay solutions were mixed for 5-10 seconds on a shaker plate, covered and incubated for 30 minutes at ambient temperature. Z-Val-Val-Arg-AMC (9 nMoles in 25 μL of assay buffer) was added to the assay solutions and hydrolysis was followed spectrophotometrically at (λ 460 nm) for 5 minutes. Apparent inhibition constants (K_i) were calculated from the enzyme progress curves using standard mathematical models.

EXAMPLE 70

Cathepsin B Assay

Solutions of test compounds in varying concentrations were prepared in 10 μL of dimethyl sulfoxide (DMSO) and then diluted into assay buffer (40 μL, comprising: *N,N*-bis(2-hydroxyethyl)-2-aminoethanesulfonic acid (BES), 50 mM (pH 6); polyoxyethylenesorbitan monolaurate, 0.05%; and dithiothreitol (DTT), 2.5 mM). Human cathepsin B (0.025 pMoles in 25 μL of assay buffer) was added to the dilutions. The assay solutions were mixed for 5-10 seconds on a shaker plate, covered and incubated for 30 minutes at ambient temperature. Z-FR-AMC (20 nMoles in 25 μL of assay buffer) was added to the assay solutions and hydrolysis was followed spectrophotometrically at (λ 460 nm) for 5 minutes. Apparent inhibition constants (K_i) were calculated from the enzyme progress curves using standard mathematical models.

EXAMPLE 71

Cathepsin K Assay

Solutions of test compounds in varying concentrations were prepared in 10 μL of dimethyl sulfoxide (DMSO) and then diluted into assay buffer (40 μL, comprising: MES, 50 mM (pH 5.5); EDTA, 2.5 mM; and DTT, 2.5 mM). Human cathepsin K (0.0906 pMoles in 25 μL of assay buffer) was added to the dilutions. The assay solutions were mixed for 5-10 seconds on a shaker plate, covered and incubated for 30 minutes at ambient temperature. Z-Phe-Arg-AMC (4 nMoles in 25 μL of assay buffer) was added to the assay solutions and hydrolysis was followed spectrophotometrically at (λ 460 nm) for 5 minutes. Apparent inhibition constants (K_i) were calculated from the enzyme progress curves using standard mathematical models.

EXAMPLE 72

Cathepsin L Assay

Solutions of test compounds in varying concentrations were prepared in 10 μL of dimethyl sulfoxide (DMSO) and then diluted into assay buffer (40 μL, comprising: MES, 50 mM (pH 5.5); EDTA, 2.5 mM; and DTT, 2.5 mM). Human cathepsin L (0.05 pMoles in 25 μL of assay buffer) was added to the dilutions. The assay solutions were mixed for 5-10 seconds on a shaker plate, covered and incubated for 30 minutes at ambient temperature. Z-Phe-Arg-AMC (1 nMoles in 25 μL of assay buffer) was added to the assay solutions and hydrolysis was followed spectrophotometrically at (λ 460 nm) for 5 minutes. Apparent inhibition constants (K_i) were calculated from the enzyme progress curves using standard mathematical models.

Compounds of the invention were tested according to the above-described assays for protease inhibition and observed to exhibit selective cathepsin S inhibitory activity. For example, the compounds of the invention were found to inhibit cathepsin S protease activity at concentrations that are least 50 fold less than those concentrations required to produce an equiactive inhibition of cathepsin K protease activity. The apparent inhibition constants (K_i) for compounds of the invention, against Cathepsin S, were in the range from about 10^{-10}M to about 10^{-7}M.

EXAMPLE 73

Representative Pharmaceutical Formulations Containing a Compound of Formula I

ORAL FORMULATION

Compound of Formula I	10-100 mg
Citric Acid Monohydrate	105 mg
Sodium Hydroxide	18 mg
Flavoring	
Water	q.s. to 100 mL

INTRAVENOUS FORMULATION

Compound of Formula I	0.1-10 mg

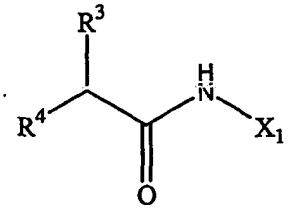
Dextrose Monohydrate	q.s. to make isotonic
Citric Acid Monohydrate	1.05 mg
Sodium Hydroxide	0.18 mg
Water for Injection	q.s. to 1.0 mL

TABLET FORMULATION

Compound of Formula I	1%
Microcrystalline Cellulose	73%
Stearic Acid	25%
Colloidal Silica	1%.

WE CLAIM:

1. A compound of Formula I:



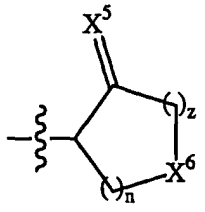
I

in which:

X^1 is $-C(R^1)(R^2)X^2$ or $-X^3$;

X^2 is cyano, -CHO, $-C(R^7)(R^8)R^5$, $-C(R^7)(R^8)CF_3$, $-C(R^7)(R^8)CF_2CF_2R^9$ $-CH{=}CHS(O)_2R^5$, $-C(R^7)(R^8)CF_2C(O)NR^5R^6$, $-C(R^7)(R^8)C(R^7)(R^8)NR^5R^6$, $-C(R^7)(R^8)C(R^7)(R^8)OR^5$, $-C(R^7)(R^8)CH_2OR^5$, $-C(R^7)(R^8)CH_2N(R^6)SO_2R^5$, $-C(R^7)(R^8)C(R^7)(R^8)N(R^6)(CH_2)_2OR^6$, $-C(R^7)(R^8)C(R^7)(R^8)N(R^6)(CH_2)_2NR^6$ or $-C(R^7)(R^8)C(R^7)(R^8)R^5$; wherein R^5 is (C_{1-4})alkyl, (C_{6-10})aryl(C_{0-6})alkyl, hetero(C_{4-10})aryl(C_{0-6})alkyl, (C_{4-10})cycloalkyl(C_{0-6})alkyl or hetero(C_{4-10})cycloalkyl(C_{0-6})alkyl; R^6 is hydrogen or (C_{1-6})alkyl; R^7 is hydrogen or (C_{1-4})alkyl and R^8 is hydroxy or R^7 and R^8 together form oxo; R^9 is hydrogen, halo, (C_{1-4})alkyl, (C_{5-10})aryl(C_{0-6})alkyl or hetero(C_{5-10})aryl(C_{0-6})alkyl;

X^3 represents a group of Formula (a):



(a)

in which n is 1 or 2, z is 0 or 1, X^5 is selected from NR^{10}, S or O, wherein R^{10} is hydrogen or (C_{1-6})alkyl, and X^6 is O, S or NR^{11}, wherein R^{11} is selected from hydrogen, (C_{1-6})alkyl, $-X^4C(O)OR^{12}$, $-X^4C(O)R^{13}$, $-X^4C(O)NR^{12}R^{12}$, $-X^4S(O)_2NR^{12}R^{12}$, $-X^4S(O)_2R^{14}$, $-R^{15}$, $-X^4S(O)_2R^{15}$, $-X^4C(O)R^{15}$, $-X^4C(O)OR^{15}$, $-X^4C(O)NR^{12}R^{15}$ and $-X^4S(O)_2NR^{12}R^{15}$, in which X^4 is a bond or (C_{1-6})alkylene; R^{12} at each occurrence independently is hydrogen or (C_{1-6})alkyl; R^{13} is hydrogen, (C_{1-6})alkyl or halo-substituted(C_{1-6})alkyl, R^{14} is (C_{1-6})alkyl or halo-substituted(C_{1-6})alkyl and R^{15} is (C_{3-10})cycloalkyl(C_{0-6})alkyl, hetero(C_{3-10})cycloalkyl(C_{0-3})alkyl, (C_{6-10})aryl(C_{0-6})alkyl, hetero(C_{5-10})aryl(C_{0-6})alkyl, (C_{9-12})bicycloaryl(C_{0-6})alkyl or hetero(C_{8-12})bicycloaryl(C_{0-6})alkyl;

wherein within X^1 any cycloalkyl, heterocycloalkyl, aryl or heteroaryl may be substituted with 1 radical R^{20} selected from $-R^{15}$, $-X^4OR^{15}$, $-X^4SR^{15}$, $-X^4S(O)R^{15}$, $-X^4S(O)_2R^{15}$, $-X^4C(O)R^{15}$, $-X^4C(O)OR^{15}$, $-X^4OC(O)R^{15}$, $-X^4NR^{15}R^{12}$, $-X^4NR^{12}C(O)R^{15}$, $-X^4NR^{12}C(O)OR^{15}$, $-X^4C(O)NR^{15}R^{12}$, $-X^4S(O)_2NR^{15}R^{12}$, $-X^4NR^{12}S(O)_2R^{15}$, $-X^4NR^{12}C(O)NR^{15}R^{12}$ and $-X^4NR^{12}C(NR^{12})NR^{15}R^{12}$; and wherein X^1 and R^{20} may be substituted further with 1 to 5 radicals independently selected from (C_{1-6})alkyl, cyano, halo, halo-substituted(C_{1-4})alkyl, nitro, $-X^4NR^{12}R^{12}$, $-X^4NR^{12}C(O)R^{12}$, $-X^4NR^{12}C(O)OR^{12}$, $-X^4NR^{12}C(O)NR^{12}R^{12}$, $-X^4NR^{12}C(NR^{12})NR^{12}R^{12}$, $-X^4OR^{13}$, $-X^4SR^{13}$, $-X^4C(O)OR^{12}$, $-X^4C(O)R^{13}$, $-X^4OC(O)R^{13}$, $-X^4C(O)NR^{12}R^{12}$, $-X^4S(O)_2NR^{12}R^{12}$, $-X^4NR^{12}S(O)_2R^{13}$, $-X^4P(O)(OR^{12})OR^{12}$, $-X^4OP(O)(OR^{12})OR^{12}$, $-X^4S(O)R^{14}$ and $-X^4S(O)_2R^{14}$ wherein X^4, R^{12}, R^{13}, R^{14} and R^{15} are as defined above;

R^1 and R^2 are both fluoro; or

R^1 is hydrogen or (C_{1-6})alkyl and R^2 is selected from the group consisting of hydrogen, (C_{1-6})alkyl, cyano, $-X^4NR^{12}R^{12}$, $-X^4NR^{12}C(O)R^{12}$, $-X^4NR^{12}C(O)OR^{12}$, $-X^4NR^{12}C(O)NR^{12}R^{12}$, $-X^4NR^{12}C(NR^{12})NR^{12}R^{12}$, $-X^4OR^{13}$, $-X^4SR^{13}$, $-X^4C(O)OR^{12}$, $-X^4C(O)R^{13}$, $-X^4OC(O)R^{13}$, $-X^4C(O)NR^{12}R^{12}$, $-X^4S(O)_2NR^{12}R^{12}$, $-X^4NR^{12}S(O)_2R^{13}$, $-X^4P(O)(OR^{12})OR^{12}$, $-X^4OP(O)(OR^{12})OR^{12}$, $-X^4S(O)R^{14}$, $-X^4S(O)_2R^{14}$, $-R^{15}$, $-X^4OR^{15}$, $-X^4SR^{15}$, $-X^4S(O)R^{15}$, $-X^4S(O)_2R^{15}$, $-X^4C(O)R^{15}$, $-X^4C(O)OR^{15}$, $-X^4OC(O)R^{15}$, $-X^4NR^{15}R^{12}$, $-X^4NR^{12}C(O)R^{15}$, $-X^4NR^{12}C(O)OR^{15}$, $-X^4C(O)NR^{15}R^{12}$, $-X^4S(O)_2NR^{15}R^{12}$, $-X^4NR^{12}S(O)_2R^{15}$, $-X^4NR^{12}C(O)NR^{15}R^{12}$ and $-X^4NR^{12}C(NR^{12})NR^{15}R^{12}$, wherein X^4, R^{12}, R^{13}, R^{14} and R^{15} are as defined above; or R^1 and R^2 taken together with the carbon atom to which both R^1 and R^2 are attached form (C_{3-8})cycloalkylene or hetero(C_{3-8})cycloalkylene;

wherein R^2, said cycloalkylene and said heterocycloalkylene may be substituted further with 1 to 3 radicals independently selected from (C_{1-6})alkyl, cyano, halo, halo-substituted(C_{1-4})alkyl, nitro, $-X^4NR^{12}R^{12}$, $-X^4NR^{12}C(O)R^{12}$, $-X^4NR^{12}C(O)OR^{12}$, $-X^4NR^{12}C(O)NR^{12}R^{12}$, $-X^4NR^{12}C(NR^{12})NR^{12}R^{12}$, $-X^4OR^{13}$, $-X^4SR^{13}$, $-X^4C(O)OR^{12}$, $-X^4C(O)R^{13}$, $-X^4OC(O)R^{13}$, $-X^4C(O)NR^{12}R^{12}$, $-X^4S(O)_2NR^{12}R^{12}$, $-X^4NR^{12}S(O)_2R^{13}$, $-X^4P(O)(OR^{12})OR^{12}$, $-X^4OP(O)(OR^{12})OR^{12}$, $-X^4S(O)R^{14}$ and $-X^4S(O)_2R^{14}$, wherein X^4, R^{12}, R^{13} and R^{14} are as defined above;

R^3 and R^4 are independently $-C(R^{16})(R^{17})X^7$, wherein R^{16} and R^{17} are hydrogen, (C_{1-6})alkyl or fluoro, or R^{16} is hydrogen and R^{17} is hydroxy and X^7 is selected from $-X^4NR^{12}R^{12}$, $-X^4NR^{12}C(O)R^{12}$, $-X^4NR^{12}C(O)OR^{12}$, $-X^4NR^{12}C(O)NR^{12}R^{12}$, $-X^4NR^{12}C(NR^{12})NR^{12}R^{12}$, $-X^4OR^{13}$, $-X^4SR^{13}$, $-X^4C(O)OR^{12}$, $-X^4C(O)R^{13}$, $-X^4OC(O)R^{13}$, $-X^4C(O)NR^{12}R^{12}$, $-X^4S(O)_2NR^{12}R^{12}$, $-X^4NR^{12}S(O)_2R^{13}$, $-X^4P(O)(OR^{12})OR^{12}$, $-X^4OP(O)(OR^{12})OR^{12}$, $-X^4S(O)R^{14}$, $-X^4S(O)_2R^{14}$, $-R^{15}$, $-X^4OR^{15}$, $-X^4SR^{15}$, $-X^4S(O)R^{15}$, $-X^4S(O)_2R^{15}$, $-X^4C(O)R^{15}$, $-X^4C(O)OR^{15}$, $-X^4OC(O)R^{15}$, $-X^4NR^{15}R^{12}$, $-X^4NR^{12}C(O)R^{15}$, $-X^4NR^{12}C(O)OR^{15}$, $-X^4C(O)NR^{15}R^{12}$, $-X^4S(O)_2NR^{15}R^{12}$, $-X^4NR^{12}S(O)_2R^{15}$, $-X^4NR^{12}C(O)NR^{15}R^{12}$ and $-X^4NR^{12}C(NR^{12})NR^{15}R^{12}$, wherein X^4, R^{12}, R^{13}, R^{14} and R^{15} are as defined above;

wherein within one of R^3 or R^4 any cycloalkyl, heterocycloalkyl, aryl or heteroaryl may be substituted with 1 radical R^{21} selected from $-R^{15}$, $-X^4OR^{15}$, $-X^4SR^{15}$, $-X^4S(O)R^{15}$, $-X^4S(O)_2R^{15}$, $-X^4C(O)R^{15}$, $-X^4C(O)OR^{15}$, $-X^4OC(O)R^{15}$, $-X^4NR^{15}R^{12}$, $-X^4NR^{12}C(O)R^{15}$, $-X^4NR^{12}C(O)OR^{15}$, $-X^4C(O)NR^{12}R^{15}$, $-X^4S(O)_2NR^{15}R^{12}$, $-X^4NR^{12}S(O)_2R^{15}$, $-X^4NR^{12}C(O)NR^{15}R^{12}$ and $-X^4NR^{12}C(NR^{12})NR^{15}R^{12}$, wherein X^4, R^{12} and R^{15} are as defined above; and wherein each of R^3, R^4 and R^{21} may be substituted further with 1 to 5 radicals independently selected from (C_{1-6})alkyl, cyano, halo, halo-substituted(C_{1-4})alkyl, nitro, $-X^4NR^{12}R^{12}$, $-X^4NR^{12}C(O)R^{12}$, $-X^4NR^{12}C(O)OR^{12}$, $-X^4NR^{12}C(O)NR^{12}R^{12}$, $-X^4NR^{12}C(NR^{12})NR^{12}R^{12}$, $-X^4OR^{13}$, $-X^4SR^{13}$, $-X^4C(O)OR^{12}$, $-X^4C(O)R^{13}$, $-X^4OC(O)R^{13}$, $-X^4C(O)NR^{12}R^{12}$, $-X^4S(O)_2NR^{12}R^{12}$, $-X^4NR^{12}S(O)_2R^{13}$, $-X^4P(O)(OR^{12})OR^{12}$, $-X^4OP(O)(OR^{12})OR^{12}$, $-X^4S(O)R^{14}$ and $-X^4S(O)_2R^{14}$, wherein X^4, R^{12}, R^{13} and R^{14} are as defined above; provided that only one bicyclic ring structure is present within each of R^3 or R^4; and provided that when X^2 is cyano and X^7 within one of R^3 or R^4 is $-X^4C(O)R^{13}$ or $-X^4C(O)R^{15}$, wherein X^4 is a bond, then X^7 within the other of R^3 or R^4 is limited to

$-X^4SR^{15}$, $-X^4S(O)R^{15}$ and $-X^4S(O)_2R^{15}$, wherein R^{15} is (C_{6-10})aryl(C_{1-6})alkyl substituted with 1 to 5 radicals or hetero(C_{5-10})aryl(C_{0-6})alkyl optionally substituted with 1 to 5 radicals, wherein said radicals are independently selected from (C_{1-6})alkyl, cyano, halo, halo-substituted(C_{1-4})alkyl, nitro, $-X^4NR^{12}R^{12}$, $-X^4NR^{12}C(O)R^{12}$, $-X^4NR^{12}C(O)OR^{12}$, $-X^4NR^{12}C(O)NR^{12}R^{12}$, $-X^4NR^{12}C(NR^{12})NR^{12}R^{12}$, $-X^4OR^{13}$, $-X^4SR^{13}$, $-X^4C(O)OR^{12}$, $-X^4C(O)R^{13}$, $-X^4OC(O)R^{13}$, $-X^4C(O)NR^{12}R^{12}$, $-X^4S(O)_2NR^{12}R^{12}$, $-X^4NR^{12}S(O)_2R^{13}$, $-X^4P(O)(OR^{12})OR^{12}$, $-X^4OP(O)(OR^{12})OR^{12}$, $-X^4S(O)R^{14}$ and $-X^4S(O)_2R^{14}$, wherein X^4, R^{12}, R^{13} and R^{14} are as defined above, provided that the radical is not selected from only halo when R^{15} is (C_{6-10})aryl(C_{1-6})alkyl; and provided that when X^2 is cyano then X^7 within R^3 and R^4 is not $-X^4C(O)NR^{12}R^{12}$, $-X^4C(O)NR^{15}R^{12}$ or $-X^4C(O)NR^{18}R^{19}$, wherein X^4 is a bond and R^{18} and R^{19} together with the nitrogen atom to which they are attached form hetero(C_{3-10})cycloalkyl or hetero(C_{5-10})aryl;

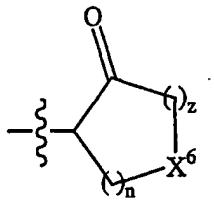
and the *N*-oxide derivatives, prodrug derivatives, protected derivatives, individual isomers and mixtures of isomers thereof; and the pharmaceutically acceptable salts and solvates of such compounds and the N-oxide derivatives, prodrug derivatives, protected derivatives, individual isomers and mixtures of isomers thereof.

2. The compound of Claim 1 in which:

X^1 is $-C(R^1)(R^2)X^2$ or $-X^3$;

X^2 is cyano, -CHO, $-C(O)R^5$, $-C(O)CF_3$, $-C(O)CF_2CF_2R^9$ $-CH{=}CHS(O)_2R^5$, $-C(O)CF_2C(O)NR^5R^6$, $-C(O)C(O)NR^5R^6$, $-C(O)C(O)OR^5$, $-C(O)CH_2OR^5$, $-C(O)CH_2N(R^6)SO_2R^5$, $-C(O)C(O)N(R^6)(CH_2)_2OR^6$, $-C(O)C(O)N(R^6)(CH_2)_2NR^6$ or $-C(O)C(O)R^5$, wherein R^5 is (C_{1-4})alkyl, (C_{6-10})aryl(C_{0-6})alkyl, hetero(C_{4-10})aryl(C_{0-6})alkyl, (C_{4-10})cycloalkyl(C_{0-6})alkyl or hetero(C_{4-10})cycloalkyl(C_{0-6})alkyl, R^6 is hydrogen or (C_{1-6})alkyl and R^9 is halo;

X^3 represents a group of Formula (b):



(b)

in which n is 1 or 2, z is 0 or 1, X^6 is O or NR^{11}, wherein R^{11} is selected from hydrogen, (C_{1-6})alkyl, $-X^4OC(O)R^{13}$, $-X^4C(O)OR^{12}$, $-X^4C(O)R^{13}$, $-X^4C(O)NR^{12}R^{12}$, $-X^4S(O)_2NR^{12}R^{12}$, $-X^4S(O)_2R^{14}$, $-R^{15}$, $-X^4S(O)_2R^{15}$, $-X^4C(O)R^{15}$, $-X^4C(O)OR^{15}$, $-X^4C(O)NR^{12}R^{15}$ and $-X^4S(O)_2NR^{12}R^{15}$, in which X^4 is a bond or (C_{1-6})alkylene; R^{12} at each occurrence independently is hydrogen or (C_{1-6})alkyl; R^{13} is hydrogen, (C_{1-6})alkyl or halo-substituted(C_{1-6})alkyl, R^{14} is (C_{1-6})alkyl or halo-substituted(C_{1-6})alkyl and R^{15} is (C_{3-10})cycloalkyl(C_{0-6})alkyl, hetero(C_{3-10})cycloalkyl(C_{0-3})alkyl, (C_{6-10})aryl(C_{0-6})alkyl, hetero(C_{5-10})aryl(C_{0-6})alkyl, (C_{9-12})bicycloaryl(C_{0-6})alkyl or hetero(C_{8-12})bicycloaryl(C_{0-6})alkyl;

wherein within X^1 any cycloalkyl, heterocycloalkyl, aryl or heteroaryl may be substituted with 1 radical selected from $-R^{15}$ and $-X^4C(O)R^{15}$; and wherein X^1 may be substituted further with 1 to 3 radicals independently selected from (C_{1-6})alkyl, halo-substituted(C_{1-4})alkyl, $-X^4NR^{12}R^{12}$, $-X^4OR^{13}$ and $-X^4S(O)_2R^{14}$, wherein X^4, R^{12}, R^{13}, R^{14} and R^{15} are as defined above;

R^1 and R^2 are both fluoro; or

R^1 is hydrogen or (C_{1-6})alkyl and R^2 is selected from the group consisting of hydrogen, (C_{1-6})alkyl, $-X^4OR^{13}$ and $-R^{15}$; or R^1 and R^2 taken together with the carbon atom to which both R^1 and R^2 are attached form (C_{3-8})cycloalkylene or hetero(C_{3-8})cycloalkylene; wherein R^2 may be substituted further with (C_{1-6})alkyl; wherein X^4, R^{13} and R^{15} are as defined above;

R^3 and R^4 are independently $-C(R^{16})(R^{17})X^7$, wherein R^{16} and R^{17} are hydrogen, (C_{1-6})alkyl or fluoro, or R^{16} is hydrogen and R^{17} is hydroxy and X^7 is selected from $-X^4SR^{13}$, $-X^4C(O)R^{13}$, $-X^4C(O)NR^{12}R^{12}$, $-R^{15}$, $-X^4OR^{15}$, $-X^4SR^{15}$, $-X^4S(O)_2R^{15}$, $-X^4C(O)R^{15}$ and $-X^4C(O)NR^{15}R^{12}$, wherein X^4, R^{12}, R^{13} and R^{15} are as defined above;

wherein within one of R^3 or R^4 any cycloalkyl, heterocycloalkyl, aryl or heteroaryl may be substituted with 1 radical selected from $-R^{15}$, $-X^4OR^{15}$, $-X^4SR^{15}$, $-X^4S(O)R^{15}$, $-X^4S(O)_2R^{15}$, $-X^4C(O)R^{15}$, $-X^4C(O)OR^{15}$, $-X^4OC(O)R^{15}$, $-X^4NR^{15}R^{12}$, $-X^4NR^{12}C(O)R^{15}$, $-X^4NR^{12}C(O)OR^{15}$, $-X^4C(O)NR^{12}R^{15}$, $-X^4S(O)_2NR^{15}R^{12}$, $-X^4NR^{12}S(O)_2R^{15}$, $-X^4NR^{12}C(O)NR^{15}R^{12}$ and $-X^4NR^{12}C(NR^{12})NR^{15}R^{12}$, wherein X^4, R^{12} and R^{15} are as defined above; and wherein each of R^3 and R^4 may be substituted further with 1 to 5 radicals independently selected from (C_{1-6})alkyl, cyano, halo, halo-substituted(C_{1-4})alkyl, nitro, $-X^4NR^{12}R^{12}$, $-X^4NR^{12}C(O)R^{12}$, $-X^4NR^{12}C(O)OR^{12}$, $-X^4NR^{12}C(O)NR^{12}R^{12}$, $-X^4NR^{12}C(NR^{12})NR^{12}R^{12}$, $-X^4OR^{13}$, $-X^4SR^{13}$, $-X^4C(O)OR^{12}$, $-X^4C(O)R^{13}$, $-X^4OC(O)R^{13}$, $-X^4C(O)NR^{12}R^{12}$, $-X^4S(O)_2NR^{12}R^{12}$, $-X^4NR^{12}S(O)_2R^{13}$, $-X^4P(O)(OR^{12})OR^{12}$, $-X^4OP(O)(OR^{12})OR^{12}$, $-X^4S(O)R^{14}$ and $-X^4S(O)_2R^{14}$, wherein X^4, R^{12}, R^{13} and R^{14} are as defined above;

wherein within one of R^3 and R^4 any cycloalkyl, heterocycloalkyl, aryl or heteroaryl may be substituted with 1 radical selected from $-R^{15}$ and $-X^4OR^{15}$; and wherein each of R^3 or R^4 may be substituted further by 1-5 radicals independently selected from (C_{1-6})alkyl, cyano, halo, halo-substituted(C_{1-4})alkyl, $-X^4NR^{12}C(O)OR^{12}$, $-X^4OR^{13}$, $-X^4C(O)OR^{12}$, $-X^4C(O)R^{13}$, $-X^4C(O)NR^{12}R^{12}$, $-X^4NR^{12}S(O)_2R^{13}$ and $-X^4S(O)_2R^{14}$, wherein X^4, R^{12}, R^{13}, R^{14} and R^{15} are as defined above;

and the *N*-oxide derivatives, prodrug derivatives, protected derivatives, individual isomers and mixtures of isomers thereof; and the pharmaceutically acceptable salts and solvates of such compounds and the N-oxide derivatives, prodrug derivatives, protected derivatives, individual isomers and mixtures of isomers thereof.

3. A compound of claim 2 in which R^3 and R^4 are independently $-CH_2X^7$, wherein X^7 is selected from X^4SR^{13}, $-X^4C(O)R^{13}$, $-X^4C(O)NR^{12}R^{12}$, $-R^{15}$, $-X^4OR^{15}$, $-X^4SR^{15}$, $-X^4S(O)_2R^{15}$, $-X^4C(O)R^{15}$ and $-X^4C(O)NR^{15}R^{12}$, wherein X^4 is a bond or (C_{1-6})alkylene, R^{12} at each occurrence independently is hydrogen or (C_{1-6})alkyl, R^{13} is hydrogen, (C_{1-6})alkyl or halo-substituted(C_{1-6})alkyl, R^{14} is (C_{1-6})alkyl or halo-substituted(C_{1-6})alkyl and R^{15} is (C_{3-10})cycloalkyl(C_{0-6})alkyl, (C_{3-10})cycloalkyl(C_{0-6})alkyl, hetero(C_{3-10})cycloalkyl(C_{0-3})alkyl, (C_{6-10})aryl(C_{0-6})alkyl, hetero(C_{5-10})aryl(C_{0-6})alkyl, (C_{9-12})bicycloaryl(C_{0-6})alkyl or

hetero(C_{8-12})bicycloaryl(C_{0-6})alkyl; wherein within R^3 and R^4 any cycloalkyl, heterocycloalkyl, aryl or heteroaryl may be substituted with 1 radical selected from $-R^{15}$ and $-X^4OR^{15}$, wherein X^4 and R^{15} are as defined above; and wherein R^3 and R^4 may be substituted further by 1 to 5 radicals independently selected from (C_{1-6})alkyl, cyano, halo, halo-substituted(C_{1-4})alkyl, $-X^4NR^{12}C(O)OR^{12}$, $-X^4OR^{13}$, $-X^4C(O)OR^{12}$, $-X^4C(O)R^{13}$, $-X^4C(O)NR^{12}R^{12}$, $-X^4NR^{12}S(O)_2R^{13}$ and $-X^4S(O)_2R^{14}$, wherein X^4 R^{12}, R^{13} and R^{14} are as defined above;

and the *N*-oxide derivatives, prodrug derivatives, protected derivatives, individual isomers and mixtures of isomers thereof; and the pharmaceutically acceptable salts and solvates of such compounds and the N-oxide derivatives, prodrug derivatives, protected derivatives, individual isomers and mixtures of isomers thereof.

4. A compound of claim 3 in which R^3 is selected from 5-bromo-thiophen-2-ylmethyl, 3-cyclohexylpropyl, 2-cyclohexylpropyl, 2-cyclopentylpropyl, 3-phenylpropyl, 3-(2-difluoromethoxy)phenylpropyl, 2-phenylcyclopropylmethyl, 2,2-difluoro-3-phenylpropyl, 1-benzylcyclopropylmethy, 2-tetrahydro-pyran-4-ylethyl, 1-isobutylcyclopropylmethyl, thiophen-2-ylmethyl, tetrahydro-pyran-4-ylmethyl, cyclopropylmethylsulfanylmethyl, 2,2-dimethyl-3-phenylpropyl, 4-methyl-[1,2,5]thiadiazol-3-ylmethylsulfonylmethyl, 3-methyl-[1,2,4]thiadiazol-3-ylmethylsulfonylmethyl, thiophen-3-ylmethylsulfonylmethyl, 3-methoxy-5-methyl-isoxazol-4-ylmethylsulfonylmethyl, 2,4-dimethyl-thiazol-5-ylmethylsulfonylmethyl, 2-methyl-oxazol-4-ylmethylsulfonylmethyl, 2-methyl-thiazol-4-ylmethylsulfonylmethyl,, 1,2,3]thiadiazol-4-ylmethylsulfonylmethyl, 3-methyl-[1,2,4]thiadiazol-5-ylmethylsulfonylmethyl, 4-methyl-[1,2,5]thiadiazol-3-ylmethylsulfonylmethyl, thiophen-3-ylmethylsulfonylmethyl, tetrahydro-pyran-4-yloxymethyl, piperidin-1-ylcarbonyl, thiophene-2-sulfonylmethyl, 3-chloro-2-fluoro-benzylsulfonylmethyl, benzenesulfonylmethyl, benzylsulfonylmethyl, 2-(1,1-difluoro-methoxy)-benzylsulfonylmethyl, 2-benzenesulfonyl-ethyl, 2-(pyridine-2-sulfonyl)-ethyl, 2-(pyridine-4-sulfonyl)-ethyl, 2-benzylsulfonyl-ethyl, oxy-pyridin-2-ylmethylsulfonylmethyl, prop-2-ene-1-sulfonylmethyl, 4-methoxy-benzylsulfonylmethyl, *p*-tolylmethylsulfonylmethyl,

4-chloro-benzylsulfonylmethyl, *o*-tolylmethylsulfonylmethyl, 3,5-dimethyl-benzylsulfonylmethyl, 4-trifluoromethyl-benzylsulfonylmethyl, 4-trifluoromethoxy-benzylsulfonylmethyl, 2-bromo-benzylsulfonylmethyl, pyridin-2-ylmethylsulfonylmethyl, pyridin-3-ylmethylsulfonylmethyl, pyridin-4-ylmethylsulfonylmethyl, naphthalen-2-ylmethylsulfonylmethyl, 3-methyl-benzylsulfonylmethyl, 3-trifluoromethyl-benzylsulfonylmethyl, 3-trifluoromethoxy-benzylsulfonylmethyl, 4-fluoro-2-trifluoromethoxy-benzylsulfonylmethyl, 2-fluoro-6-trifluoromethyl-benzylsulfonylmethyl, 3-chloro-benzylsulfonylmethyl, 2-fluoro-benzylsulfonylmethyl, 2-trifluoro-benzylsulfonylmethyl, 2-cyano-benzylsulfonylmethyl, 4-*tert*-butyl-benzylsulfonylmethyl, 2-fluoro-3-methyl-benzylsulfonylmethyl, 3-fluoro-benzylsulfonylmethyl, 4-fluoro-benzylsulfonylmethyl, 2-chloro-benzylsulfonylmethyl, 2,5-difluoro-benzylsulfonylmethyl, 2,6-difluoro-benzylsulfonylmethyl, 2,5-dichloro-benzylsulfonylmethyl, 3,4-dichloro-benzylsulfonylmethyl, 2-(1,1-difluoro-methoxy)-benzylsulfonylmethyl, 2-cyano-benzylsulfonylmethyl, 3-cyano-benzylsulfonylmethyl, 2-trifluoromethoxy-benzylsulfonylmethyl, 2,3-difluoro-benzylsulfonylmethyl, 2,5-difluoro-benzylsulfonylmethyl, biphenyl-2-ylmethylsulfonylmethyl, cyclohexylmethyl, 3-fluoro-benzylsulfonylmethyl, 3,4-difluoro-benzylsulfonylmethyl, 2,4-difluoro-benzylsulfonylmethyl, 2,4,6-trifluoro-benzylsulfonylmethyl, 2,4,5-trifluoro-benzylsulfonylmethyl, 2,3,4-trifluoro-benzylsulfonylmethyl, 2,3,5-trifluoro-benzylsulfonylmethyl, 2,5,6-trifluoro-benzylsulfonylmethyl, 2-chloro-5-trifluoromethylbenzylsulfonylmethyl, 2-methyl-propane-1-sulfonyl, 2-fluoro-3-trifluoromethylbenzylsulfonylmethyl, 2-fluoro-4-trifluoromethylbenzylsulfonylmethyl, 2-fluoro-5-trifluoromethylbenzylsulfonylmethyl, 4-fluoro-3-trifluoromethylbenzylsulfonylmethyl, 2-methoxy-benzylsulfonylmethyl, 3,5 bis-trifluoromethyl-benzylsulfonylmethyl, 4-difluoromethoxy-benzylsulfonylmethyl, 2-difluoromethoxy-benzylsulfonylmethyl, 3-difluoromethoxy-benzylsulfonylmethyl, 2,6-dichloro-benzylsulfonylmethyl, biphenyl-4-ylmethylsulfonylmethyl, 3,5-dimethyl-isoxazol-4-ylmethylsulfonylmethyl,

5-chloro-thiophen-2-ylmethylsulfonylmethyl,
2-[4-(1,1-Difluoro-methoxy)-benzenesulfonyl]-ethyl,
2-[2-(1,1-Difluoro-methoxy)-benzenesulfonyl]-ethyl,
2-[3-(1,1-Difluoro-methoxy)-benzenesulfonyl]-ethyl,
2-(4-trifluoromethoxy-benzenesulfonyl)-ethyl,
2-(3-trifluoromethoxy-benzenesulfonyl)-ethyl,
2-(2-trifluoromethoxy-benzenesulfonyl)-ethyl, (cyanomethyl-methyl-carbamoyl)-methyl, biphenyl-3-ylmethyl, 2-oxo-2-pyrrolidin-1-yl-ethyl, 2-benzenesulfonyl-ethyl, isobutylsulfanylmethyl, 2-phenylsulfanyl-ethyl, cyclohexylmethylsulfonylmethyl, 2-cyclohexyl-ethanesulfonyl, benzyl, naphthalen-2-yl, benzylsulfanylmethyl, 2-trifluoromethyl-benzylsulfanylmethyl, phenylsulfanyl-ethyl and cyclopropylmethylsulfonylmethyl;

and the *N*-oxide derivatives, prodrug derivatives, protected derivatives, individual isomers and mixtures of isomers thereof; and the pharmaceutically acceptable salts and solvates of such compounds and the N-oxide derivatives, prodrug derivatives, protected derivatives, individual isomers and mixtures of isomers thereof.

5. A compound of claim 4 in which R^4 is selected from 2-trifluorobenzylsulfonylmethyl, 3-phenylsulfanylpropyl, 4-chlorobenzylsulfonylmethyl, thiophen-2-ylsulfonylmethyl, benzylsulfonylmethyl, 4-methylbenzylsulfonylmethyl, 2-phenylsulfonylethyl, 2-pyridin-2-ylsulfonylethyl, 2-pyridin-4-ylsulfonylethyl, 2-benzylsulfonylethyl, 2-(3-difluoromethoxyphenylsulfonyl)ethyl, naphthalen-2-ylmethylsulfonylmethyl, pyridin-2-ylmethylsulfonylmethyl, 3-methylbenzylsulfonylmethyl, 3-trifluoromethylbenzylsulfonylmethyl, 3-difluoromethoxybenzylsulfonylmethyl, 3-chlorobenzylsulfonylmethyl, 3-fluorobenzylsulfonylmethyl, 4-fluorobenzylsulfonylmethyl, 3-cyanobenzylsulfonylmethyl, 4-cyanobenzylsulfonylmethyl, 3,4-difluorobenzylsulfonylmethyl, benzylsulfonylmethyl, *N*-cyanomethyl-*N*-methylcarbamoylmethyl, 3-bromobenzyl, 4-phenylbutyl, 2,2-difluoro-3-phenylpropyl, 4'-methylsulfonylaminobiphenyl-3-ylmethyl, 4'-ethoxycarbonylaminobiphenyl-3-ylmethyl, 4-methylpiperazin-1-ylcarbonylmethyl,

1-fluoro-2-(4-methylpiperazin-1-yl)-2-oxoethyl, 1-hydroxy-4-methylpiperazin-1-yl-2-oxoethyl, 1-hydroxy-2-morpholin-4-yl-2-oxoethyl, 1-hydroxy-2-oxo-2-pyrrolidin-1-yl-ethyl, 1-fluoro-2-oxo-2-pyrrolidin-1-yl-ethyl, 1-fluoro-2-isopropylamino-2-oxoethyl, 1-hydroxy-2-isopropylamino-2-oxoethyl, 1-fluoro-2-oxo-2-piperazin-1-ylethyl, thiophen-3-ylmethylsulfonylmethyl, 4-methyl-[1,2,5]thiadiazol-3-ylmethylsulfonylmethyl, 3-methoxy-5-methyl-isoxazol-4-ylmethylsulfonylmethyl, 2,4-dimethyl-thiazol-5-ylmethylsulfonylmethyl, 2-methyl-oxazol-4-ylmethylsulfonylmethyl, 2-methyl-thiazol-4-ylmethylsulfonylmethyl, 2-([1,2,3]thiadiazol-4-ylmethylsulfonyl)-ethyl, 2-(3-methyl-[1,2,4]thiadiazol-5-ylmethylsulfonyl)-ethyl, 2-oxo-2-phenyl-ethyl, 2-morpholin-4-yl-2-oxo-ethyl, 2-benzenesulfonyl-ethyl, 2-naphthalen-2-yl-2-oxo-ethyl, 2-benzo[1,3]dioxol-5-yl-2-oxo-ethyl, 2-benzo[*b*]thiophen-2-yl-2-oxo-ethyl, 2-biphenyl-4-yl-2-oxo-ethyl, 4-benzylsulfonylmethyl, 2-(3-trifluoromethoxy-benzenesulfonyl)-ethyl, 2-oxo-2-(4-phenoxy-phenyl)-ethyl, 2-(4-hydroxy-phenyl)-2-oxo-ethyl, benzylcarbamoyl-methyl, 4-acetyl-piperazine-1-carboxylic acid ethyl ester, cyclohexylcarbamoylmethyl, 2-(3-Chloro-benzo[*b*]thiophen-2-yl)-2-oxo-ethyl, benzenesulfonylmethyl, 2-oxo-2-thiophen-2-yl-ethyl, 2-oxo-2-thiophen-3-yl-ethyl, naphthalene-2-sulfonylmethyl, 2-(5-methyl-thiophen-2-yl)-2-oxo-ethyl, 2-(3-chloro-thiophen-2-yl)-2-oxo-ethyl, 5-methyl-thiophene-2-sulfonylmethyl, phenylcarbamoylmethyl, (5,6,7,8-tetrahydro-naphthalen-1-ylcarbamoyl)-methyl, (4-carbamoyl-phenylcarbamoyl)-methyl, (3-carbamoyl-phenylcarbamoyl)-methyl, (butyl-methyl-carbamoyl)-methyl, biphenyl-4-ylmethyl, 2-oxo-2-*p*-tolyl-ethyl, 2-(3-fluoro-4-methoxy-phenyl)-2-oxo-ethyl, 2-(4-chloro-phenyl)-2-oxo-ethyl, 2-(4-methoxy-phenyl)-2-oxo-ethyl, 2-oxo-2-(4-trifluoromethoxy-phenyl)-ethyl, 2-(3,4-difluoro-phenyl)-2-oxo-ethyl, 2-(3,4-dimethoxy-phenyl)-2-oxo-ethyl, 2-(4-fluoro-phenyl)-2-oxo-ethyl, 5-methyl-2-oxo-hexyl, 3,5-dimethyl-benzylsulfonylmethyl, 4-trifluoromethyl-benzylsulfonylmethyl; 4-trifluoromethoxy-benzylsulfonylmethyl, isopropylcarbamoyl-methyl, 4-dimethylcarbamoylmethyl, pyridin-4-ylcarbamoylmethyl, pyridin-4-ylmethylsulfonylmethyl, pyridin-3-ylmethylsulfonylmethyl, 3,4-dichloro-benzylsulfonylmethyl, pyridin-3-ylcarbamoylmethyl,

4-methoxy-benzylsulfonylmethyl, 4-chloro-benzylsulfonylmethyl, thiophene-2-sulfonylmethyl, benzylsulfonylmethyl, *p*-tolylmethylsulfonylmethyl, 2-benzenesulfonyl-ethyl, 2-(pyridine-2-sulfonyl)-ethyl, 2-(pyridine-4-sulfonyl)-ethyl, 2-benzylsulfonyl-ethyl, 2-[3-(1,1-Difluoro-methoxy)-benzenesulfonyl]-ethyl, naphthalen-2-ylmethylsulfonylmethyl, pyridin-2-ylmethylsulfonylmethyl, *m*-tolylmethylsulfonylmethyl, 3-trifluoromethyl-benzylsulfonylmethyl, 3-trifluoromethoxy-benzylsulfonylmethyl, 3-chloro-benzylsulfonylmethyl, 3-fluoro-benzylsulfonylmethyl, 4-fluoro-benzylsulfonylmethyl, 3-cyano-benzylsulfonylmethyl, 4-cyano-benzylsulfonylmethyl, 3,4-difluoro-benzylsulfonylmethyl, (cyanomethyl-methyl-carbamoyl)-methyl, 3-bromo-benzyl, 2-oxo-2-pyrrolidin-1-yl-ethyl, 2-(4'-chloro-biphenyl-4-yl)-2-oxo-ethyl, biphenyl-3-ylmethyl, 2-(1,1-difluoro-methoxy)-benzylsulfonylmethyl, 2-(4-methylsulfonylamino-phenyl)-2-oxo-ethyl, 2-oxo-2-piperidin-1-yl-ethyl, 2-(4-methylsulfonyl-piperazin-1-yl)-2-oxo-ethyl, 2-trifluoromethyl-benzylsulfonylmethyl, 4-fluoro-3-trifluoromethyl-benzylsulfonylmethyl, 4-carboxy-benzylsulfonylmethyl, 3,5-bis-trifluoromethyl-benzylsulfonylmethyl, 4-(1,1-difluoro-methoxy)-benzylsulfonylmethyl, 3-(1,1-difluoro-methoxy)-benzylsulfonylmethyl, 5-chloro-thiophen-2-ylmethylsulfonylmethyl, 2-[4-(1,1-difluoro-methoxy)-benzenesulfonyl]-ethyl, 2-(4-trifluoromethoxy-benzenesulfonyl)-ethyl, 2-phenylsulfanyl-ethyl, benzylsulfanylmethyl, 2-trifluoromethyl-benzylsulfanylmethyl, 2-trifluoromethoxy-benzylsulfanylmethyl, 2-cyclohexyl-ethyl and isobutylsulfanylmethyl;

and the *N*-oxide derivatives, prodrug derivatives, protected derivatives, individual isomers and mixtures of isomers thereof; and the pharmaceutically acceptable salts and solvates of such compounds and the N-oxide derivatives, prodrug derivatives, protected derivatives, individual isomers and mixtures of isomers thereof.

6. The compound of claim 5 in which R^1 is hydrogen or (C_{1-6})alkyl and R^2 is hydrogen, $-X^4OR^{13}$, hetero(C_{5-10})aryl(C_{0-6})alkyl, (C_{5-10})aryl(C_{0-6})alkyl or (C_{1-6})alkyl; or R^1 and R^2 taken together with the carbon atom to which both R^1 and R^2 are attached form

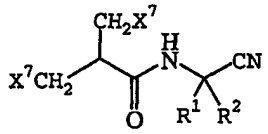
(C_{3-8})cycloalkylene or hetero(C_{3-8})cycloalkylene; wherein the cycloalkylene or heterocycloalkylene are optionally substituted with 1 to 3 (C_{1-6})alkyl radicals;

and the *N*-oxide derivatives, prodrug derivatives, protected derivatives, individual isomers and mixtures of isomers thereof; and the pharmaceutically acceptable salts and solvates of such compounds and the N-oxide derivatives, prodrug derivatives, protected derivatives, individual isomers and mixtures of isomers thereof.

7. The compound of claim 6 in which R^1 is hydrogen or methyl and R^2 is methoxymethyl, methoxyethyl, methyl, ethyl, propyl, butyl, phenethyl, hiophen-2-yl or 5-methyl-furan-2-yl; or R^1 and R^2 taken together with the carbon atom to which both R^1 and R^2 are attached form cyclopropyl, tetrahydro-pyran-4-yl or 1-methyl-piperidin-4-yl;

and the *N*-oxide derivatives, prodrug derivatives, protected derivatives, individual isomers and mixtures of isomers thereof; and the pharmaceutically acceptable salts and solvates of such compounds and the N-oxide derivatives, prodrug derivatives, protected derivatives, individual isomers and mixtures of isomers thereof.

8. The compound of claim 7 of Formula I(a):



I(a)

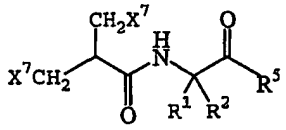
and the *N*-oxide derivatives, prodrug derivatives, protected derivatives, individual isomers and mixtures of isomers thereof; and the pharmaceutically acceptable salts and solvates of such compounds and the N-oxide derivatives, prodrug derivatives, protected derivatives, individual isomers and mixtures of isomers thereof.

9. The compound of claim 8 selected from the group consisting of 3-biphenyl-3-yl-*N*-cyanomethyl-2-benzylsulfonylmethyl-propionamide; 3-biphenyl-4-yl-*N*-

cyanomethyl-2-benzylsulfonylmethyl-propionamide; 3-(3-bromo-phenyl)-*N*-cyanomethyl-2-benzylsulfonylmethyl-propionamide; *N*-cyanomethyl-3-(3-cyano-benzylsulfonyl)-2-benzylsulfonyl-methyl-propionamide; *N*-cyanomethyl-2-[2-1,1-difluoro-methoxy)-benzylsulfanylmethyl]-3-benzylsulfanyl-propionamide; *N*-cyanomethyl-3-(2-trifluoromethyl-benzylsulfanyl)-2-(2-trifluoro-methyl-benzylsulfanylmethyl)-propionamide; *N*-cyanomethyl-3-isobutylsulfanyl-2-isobutylsulfanylmethyl-propionamide; *N*-cyanomethyl-4-phenylsulfanyl-2-(2-phenylsulfanyl-ethyl)-butyramide; *N*-cyanomethyl-3-[2-(1,1-difluoro-methoxy)-benzylsulfanyl]-2-[2-(1,1-difluoro-methoxy)-benzylsulfanylmethyl]-propionamide; 3-benzylsulfanyl-2-benzylsulfanylmethyl-*N*-cyanomethyl-propionamide; *N*-cyanomethyl-2-[2-1,1-difluoro-methoxy)-benzylsulfonylmethyl]-3-benzylsulfonyl-propionamide; *N*-cyanomethyl-3-(2-trifluoromethyl-benzylsulfonyl)-2-(2-trifluoromethyl-benzylsulfonylmethyl)-propionamide; 4-benzenesulfonyl-2-(2-benzenesulfonyl-ethyl)-*N*-cyanomethyl-butyramide; *N*-cyanomethyl-3-[2-(1,1-difluoro-methoxy)-benzylsulfonyl]-2-[2-(1,1-difluoro-methoxy)-benzylsulfonylmethyl]-propionamide; *N*-cyanomethyl-3-benzylsulfonyl-2-benzylsulfonylmethyl-propionamide; *N*-cyanomethyl-3-(2-methyl-propane-1-sulfonyl)-2-(2-methyl-propane-1-sulfonylmethyl)-propionamide; *N*-cyanomethyl-3-(2-methyl-thiazol-4-ylmethylsulfonyl)-2-benzyl-sulfonylmethyl-propionamide; 3-biphenyl-3-yl-*N*-cyanomethyl-2-[2-(1,1-difluoro-methoxy)-benzyl-sulfonylmethyl]-propionamide; (3'-{2-(cyanomethyl-carbamoyl)-3-[2-(1,1-difluoro-methoxy)-benzyl-sulfonyl]-propyl}-biphenyl-4-yl)-carbamic acid ethyl ester; *N*-cyanomethyl-2-[2-(1,1-difluoro-methoxy)-benzylsulfonylmethyl]-3-(4'-methylsulfonylamino-biphenyl-3-yl)-propionamide; 3-(3-bromo-phenyl)-*N*-cyanomethyl-2-[2-(1,1-difluoro-methoxy)-phenyl-methylsulfonylmethyl]-propionamide; *N*-cyanomethyl-2-((E)-3-phenyl-allyl)-3-benzylsulfonyl-propionamide; and *N*-cyanomethyl-3-benzylsulfonyl-2-(3-phenyl-propyl)-propionamide;

and the *N*-oxide derivatives, prodrug derivatives, protected derivatives, individual isomers and mixtures of isomers thereof; and the pharmaceutically acceptable salts and solvates of such compounds and the N-oxide derivatives, prodrug derivatives, protected derivatives, individual isomers and mixtures of isomers thereof.

10. The compound of Claim 7 of Formula I(b):



I(b)

and the *N*-oxide derivatives, prodrug derivatives, protected derivatives, individual isomers and mixtures of isomers thereof; and the pharmaceutically acceptable salts and solvates of such compounds and the N-oxide derivatives, prodrug derivatives, protected derivatives, individual isomers and mixtures of isomers thereof.

11. The compound of claim 10 in which R^5 is 1*H*-benzoimidazol-2-yl, benzooxazol-2-yl, oxazolo[4,5-b]pyridin-2-yl, benzothiazol-2-yl, 5-phenyl-[1,3,4]oxadiazol-2-yl, 4-(5-pyridin-4-yl-[1,3,4]oxadiazol-2-yl, 5-pyridin-3-yl-[1,3,4]oxadiazol-2-yl, 5-pyridazin-3-yl-[1,3,4]oxadiazol-2-yl, pyrimidin-2-yl, pyridazin-3-yl, 3-penyl-[1,2,4]oxadiazol-5-yl, 5-methoxymethyl-[1,3,4]oxadiazol-2-yl, 5-ethyl-[1,3,4]oxadiazol-2-yl,, 1,3,4]thiadiazol-2-yl, benzyloxycarbonyl, benzyloxydicarbonyl, phenyldicarbonyl, 5-methyl-[1,3,4]thiadiazol-2-yl, 5-trifluoromethyl-[1,3,4]oxadiazol-2-yl, 5-methyl-[1,3,4]oxadiazol-2-yl, 5-methyl-[1,2,4]oxadiazol-3-yl, 5-phenyl-[1,2,4]oxadiazol-3-yl, 5-thiophen-3-yl-[1,2,4]oxadiazol-3-yl, 5-trifluoromethyl-[1,2,4]oxadiazol-3-yl, 3-methyl-[1,2,4]oxadiazol-5-yl or 3-pyrazin-2-yl;

and the *N*-oxide derivatives, prodrug derivatives, protected derivatives, individual isomers and mixtures of isomers thereof; and the pharmaceutically acceptable salts and solvates of such compounds and the N-oxide derivatives, prodrug derivatives, protected derivatives, individual isomers and mixtures of isomers thereof.

12. The compound of claim 11 selected from the group consisting of *N*-[(S)-1-(1-Benzooxazol-2-yl-methanoyl)-butyl]-3-benzylsulfonyl-2-benzylsulfonylmethyl-propionamide; *N*-[(S)-1-(1-Benzooxazol-2-yl-methanoyl)-butyl]-3-(2-trifluoromethyl-benzylsulfonyl)-2-(2-trifluoromethyl-benzylsulfonylmethyl)-propionamide; *N*-[(S)-1-(1-

Benzooxazol-2-yl-methanoyl)-pentyl]-4-(2-methoxy-benzenesulfonyl)-2-[2-(2-methoxy-benzenesulfonyl)-ethyl]-butyramide; 4-Benzenesulfonyl-2-(2-benzenesulfonyl-ethyl)-*N*-[(S)-1-(1-benzooxazol-2-yl-methanoyl)-butyl]-butyramide; (R)-*N*-[(S)-1-(1-benzooxazol-2-yl-methanoyl)-butyl]-2-cyclohexylmethyl-3-benzylsulfonyl-propionamide; *N*-[(S)-1-(1-benzothiazol-2-yl-methanoyl)-propyl]-4-morpholin-4-yl-4-oxo-2-benzylsulfonylmethyl-butyramide; *N*-[(S)-1-(1-benzooxazol-2-yl-methanoyl)-butyl]-3-cyclohexyl-2-cyclohexylmethyl-propionamide; *N*-[(S)-1-(1-Benzooxazol-2-yl-methanoyl)-butyl]-3-isobutylsulfanyl-2-isobutylsulfanylmethyl-propionamide; *N*-[(S)-1-(1-benzooxazol-2-yl-methanoyl)-butyl]-3-benzylsulfanyl-2-benzylsulfanylmethyl-propionamide; *N*-[(S)-1-(1-benzooxazol-2-yl-methanoyl)-butyl]-4-phenylsulfanyl-2-(2-phenylsulfanyl-ethyl)-butyramide; *N*-[(S)-1-(1-benzooxazol-2-yl-methanoyl)-propyl]-4-morpholin-4-yl-4-oxo-2-benzylsulfonylmethyl-butyramide; *N*-[(S)-1-(1-Benzooxazol-2-yl-methanoyl)-pentyl]-4-morpholin-4-yl-4-oxo-2-benzylsulfonylmethyl-butyramide; 4-Morpholin-4-yl-4-oxo-2-benzylsulfonylmethyl-*N*-{(S)-1-[1-(3-phenyl-[1,2,4]oxadiazol-5-yl)-methanoyl]-propyl}-butyramide; *N*-[(S)-1-(1-Benzooxazol-2-yl-methanoyl)-butyl]-2-[2-(1,1-difluoro-methoxy)-benzylsulfonylmethyl]-3-benzylsulfonyl-propionamide; 4-Morpholin-4-yl-4-oxo-*N*-[1-(2-oxo-2-phenyl-acetyl)-pentyl]-2-benzylsulfonylmethyl-butyramide; *N*-(1,1-Dimethyl-2-oxazolo[4,5-b]pyridin-2-yl-2-oxo-ethyl)-4-morpholin-4-yl-4-oxo-2-benzylsulfonylmethyl-butyramide; *N*-[1-(5-Ethyl-[1,3,4]oxadiazole-2-carbonyl)-butyl]-4-morpholin-4-yl-4-oxo-2-benzylsulfonylmethyl-butyramide; *N*-[1-(5-Ethyl-[1,3,4]oxadiazole-2-carbonyl)-butyl]-4-oxo-2-benzylsulfonyl-methyl-4-piperidin-1-yl-butyramide; *N*-[1-(5-Ethyl-[1,3,4]oxadiazole-2-carbonyl)-butyl]-4-oxo-2-benzylsulfonyl-methyl-4-pyrrolidin-1-yl-butyramide; *N*-[1-(5-Methoxymethyl-[1,3,4]oxadiazole-2-carbonyl)-propyl]-4-morpholin-4-yl-4-oxo-2-benzylsulfonylmethyl-butyramide; *N*-[1-(5-Methoxymethyl-[1,3,4]oxadiazole-2-carbonyl)-propyl]-4-oxo-2-benzylsulfonylmethyl-4-piperidin-1-yl-butyramide; *N*-[1-(5-Methoxymethyl-[1,3,4]oxadiazole-2-carbonyl)-propyl]-4-oxo-2-benzylsulfonylmethyl-4-pyrrolidin-1-yl-butyramide; 4-Morpholin-4-yl-4-oxo-2-benzylsulfonylmethyl-*N*-[1-(5-phenyl-[1,3,4]oxadiazole-2-carbonyl)-propyl]-butyramide; 4-Oxo-2-benzylsulfonylmethyl-*N*-[1-(5-phenyl-[1,3,4]oxadiazole-2-carbonyl)-propyl]-4-piperidin-1-yl-butyramide; 4-Oxo-2-benzylsulfonylmethyl-*N*-[1-(5-phenyl-[1,3,4]oxadiazole-2-carbonyl)-propyl]-4-pyrrolidin-1-yl-butyramide; 4-Morpholin-4-yl-*N*-

[1-(oxazolo[4,5-b]pyridine-2-carbonyl)-propyl]-4-oxo-2-benzylsulfonylmethyl-butyramide; *N*-[1-(Oxazolo[4,5-b]pyridine-2-carbonyl)-propyl]-4-oxo-2-benzylsulfonyl-methyl-4-piperidin-1-yl-butyramide; *N*-[1-(Oxazolo[4,5-b]pyridine-2-carbonyl)-propyl]-4-oxo-2-benzylsulfonyl-methyl-4-pyrrolidin-1-yl-butyramide; 4-Morpholin-4-yl-4-oxo-2-benzylsulfonylmethyl-*N*-[1-(5-pyridin-4-yl-[1,3,4]oxadiazole-2-carbonyl)-propyl]-butyramide; 4-Oxo-2-benzylsulfonylmethyl-4-piperidin-1-yl-*N*-[1-(5-pyridin-4-yl-[1,3,4]oxadiazole-2-carbonyl)-propyl]-butyramide; 4-Oxo-2-benzylsulfonylmethyl-*N*-[1-(5-pyridin-4-yl-[1,3,4]oxadiazole-2-carbonyl)-propyl]-4-pyrrolidin-1-yl-butyramide; 4-Morpholin-4-yl-4-oxo-2-benzylsulfonylmethyl-*N*-[1-(5-pyridin-3-yl-[1,3,4]oxadiazole-2-carbonyl)-propyl]-butyramide; *N*-[1-(Benzooxazole-2-carbonyl)-propyl]-4-oxo-2-benzylsulfonylmethyl-4-piperidin-1-yl-butyramide; *N*-[1-(Benzooxazole-2-carbonyl)-propyl]-4-oxo-2-benzylsulfonylmethyl-4-pyrrolidin-1-yl-butyramide; *N*-[1-(Benzooxazole-2-carbonyl)-propyl]-2-cyclohexylmethyl-4-morpholin-4-yl-4-oxo-butyramide; 2-Cyclohexylmethyl-4-morpholin-4-yl-*N*-[1-(oxazolo[4,5-b]pyridine-2-carbonyl)-propyl]-4-oxo-butyramide; 2-Cyclohexylmethyl-N-[1-(5-ethyl-[1,3,4]oxadiazole-2-carbonyl)-butyl]-4-morpholin-4-yl-4-oxo-butyramide; *N*-(2-Benzooxazol-2-yl-1-methoxymethyl-2-oxo-ethyl)-2-(2-difluoromethoxy-benzylsulfonylmethyl)-4-morpholin-4-yl-4-oxo-butyramide; *N*-[1-(Benzooxazole-2-carbonyl)-propyl]-2-(2-cyclohexyl-ethyl)-4-morpholin-4-yl-4-oxo-butyramide; 2-(2-Cyclohexyl-ethyl)-4-morpholin-4-yl-*N*-[1-(oxazolo[4,5-b]pyridine-2-carbonyl)-propyl]-4-oxo-butyramide; 2-(2-Cyclohexyl-ethyl)-4-morpholin-4-yl-4-oxo-*N*-[1-(5-phenyl-[1,3,4]oxadiazole-2-carbonyl)-propyl]-butyramide; 2-(2-Difluoromethoxy-benzylsulfonylmethyl)-4-morpholin-4-yl-4-oxo-*N*-[1-(5-phenyl-[1,3,4]oxadiazole-2-carbonyl)-propyl]-butyramide; 2-(2-Difluoromethoxy-benzylsulfonylmethyl)-*N*-[1-(5-ethyl-[1,3,4]oxadiazole-2-carbonyl)-butyl]-4-morpholin-4-yl-4-oxo-butyramide; *N*-[1-(Benzooxazole-2-carbonyl)-propyl]-2-(2-difluoromethoxy-benzyl-sulfonylmethyl)-4-morpholin-4-yl-4-oxo-butyramide;

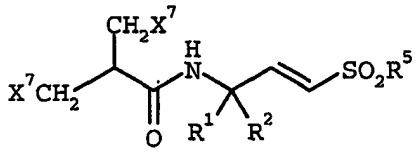
2-(2-Morpholin-4-yl-2-oxo-ethyl)-5-phenyl-pentanoic acid, 1-(benzooxazole-2-carbonyl)-propyl]-amide; (R)-2-Cyclohexylmethyl-4-morpholin-4-yl-4-oxo-*N*-[(S)-1-(5-phenyl-1,2,4-oxadiazole-3-carbonyl)-propyl]-butyramide; 2-(2-Morpholin-4-yl-2-oxo-ethyl)-5-phenyl-pentanoic acid, (S)-1-(5-phenyl-[1,2,4]oxadiazole-3-carbonyl)-propyl]-amide; 4-Morpholin-4-yl-4-oxo-2-benzylsulfonylmethyl-*N*-[(S)-1-(5-phenyl-1,2,4-

oxadiazole-3-carbonyl)-propyl]-butyramide; (R)-2-Cyclohexylmethyl-4-morpholin-4-yl-4-oxo-*N*-[(S)-1-(3-phenyl-1,2,4-oxadiazole-5-carbonyl)-propyl]-butyramide; 4-Morpholin-4-yl-*N*-[1-(oxazole-2-carbonyl)-3-phenyl-propyl]-4-oxo-2-benzylsulfonylmethyl-butyramide; *N*-(1,1-Dimethyl-2-oxazol-2-yl-2-oxo-ethyl)-4-morpholin-4-yl-4-oxo-2-benzylsulfonylmethyl-butyramide; *N*-4-Isopropyl-*N*-1-[1-(oxazole-2-carbonyl)-3-phenyl-propyl]-2-benzylsulfonylmethyl-succinamide; 2-(2-Difluoromethoxy-benzylsulfonylmethyl)-4-morpholin-4-yl-*N*-[1-(oxazole-2-carbonyl)-3-phenyl-propyl]-4-oxo-butyramide; 2-(2-Methyl-propane-1-sulfonylmethyl)-4-morpholin-4-yl-*N*-[1-(oxazole-2-carbonyl)-3-phenyl-propyl]-4-oxo-butyramide; 2-Cyclopropylmethylsulfonylmethyl-4-morpholin-4-yl-*N*-[1-(oxazole-2-carbonyl)-3-phenyl-propyl]-4-oxo-butyramide; *N*-[1-(Benzooxazole-2-carbonyl)-butyl]-2-benzylsulfonyl-3-(tetrahydro-pyran-4-yloxymethyl)-propionamide; *N*-[1-(Benzooxazole-2-carbonyl)-butyl]-3-ethanesulfonyl-2-(tetrahydro-pyran-4-yloxymethyl)-propionamide; *N*-(1-Benzenesulfonyl-3-oxo-azepan-4-yl)-2-cyclopropylmethylsulfonyl-methyl-4-morpholin-4-yl-4-oxo-butyramide; 2-Cyclopropylmethylsulfonylmethyl-N-{(S)-1-[(R)-hydroxy-(3-phenyl-1,2,4-oxadiazol-5-yl)-methyl]-propyl}-4-morpholin-4-yl-4-oxo-butyramide; *N*-{(S)-1-[(R)-hydroxy-(3-phenyl-1,2,4-oxadiazol-5-yl)-methyl]-propyl}-2-(2-methyl-propane-1-sulfonylmethyl)-4-morpholin-4-yl-4-oxo-butyramide; 2-(2-Morpholin-4-yl-2-oxo-ethyl)-5-phenyl-pentanoic acid {(S)-1-[(R)-hydroxy-(3-phenyl-1,2,4-oxadiazol-5-yl)-methyl]-propyl}-amide; 2-Cyclopropylmethylsulfonylmethyl-4-morpholin-4-yl-4-oxo-N-[(S)-1-(3-phenyl-1,2,4-oxadiazole-5-carbonyl)-propyl]-butyramide; 2-(2-methyl-propane-1-sulfonylmethyl)-4-morpholin-4-yl-4-oxo-N-[(S)-1-(3-phenyl-1,2,4-oxadiazole-5-carbonyl)-propyl]-butyramide; 2-(2-Morpholin-4-yl-2-oxo-ethyl)-5-phenyl-pentanoic acid, (S)-1-(3-phenyl-1,2,4-oxadiazole-5-carbonyl)-propyl}-amide; *N*-[(1S)-1-(Benzooxazol-2-yl-hydroxy-methyl)-3-phenyl-propyl]-2-cyclopropylmethylsulfonylmethyl-4-morpholin-4-yl-4-oxo-butyramide; (R)-2-((S)-1-Hydroxy-2-morpholin-4-yl-2-oxo-ethyl)-5-phenyl-pentanoic acid, 1-(benzoxazole-2-carbonyl)-propyl]-amide; (R)-5-(2-Difluoromethoxy-phenyl)-2-((S)-1-hydroxy-2-morpholin-4-yl-2-oxo-ethyl)-pentanoic acid, 1-(benzoxazole-2-carbonyl)-propyl]-amide; and 4-Morpholin-4-yl-N-[1-(oxazole-2-carbonyl)-cyclopropyl]-4-oxo-2-benzylsulfonyl methyl –butyramide;

and the *N*-oxide derivatives, prodrug derivatives, protected derivatives, individual

isomers and mixtures of isomers thereof; and the pharmaceutically acceptable salts and solvates of such compounds and the N-oxide derivatives, prodrug derivatives, protected derivatives, individual isomers and mixtures of isomers thereof.

13. The compound of claim 7 of Formula I(c):



I(c)

and the *N*-oxide derivatives, prodrug derivatives, protected derivatives, individual isomers and mixtures of isomers thereof; and the pharmaceutically acceptable salts and solvates of such compounds and the N-oxide derivatives, prodrug derivatives, protected derivatives, individual isomers and mixtures of isomers thereof.

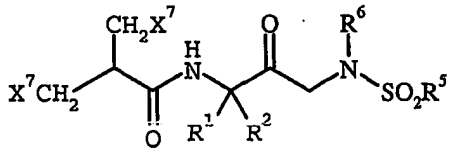
14. The compound of claim 13 in which R^5 is phenyl;

and the *N*-oxide derivatives, prodrug derivatives, protected derivatives, individual isomers and mixtures of isomers thereof; and the pharmaceutically acceptable salts and solvates of such compounds and the N-oxide derivatives, prodrug derivatives, protected derivatives, individual isomers and mixtures of isomers thereof.

15. The compound of claim 14 selected from the group consisting of *N*-[(S)-1-((E)-2-benzenesulfonyl-vinyl)-pentyl]-3-benzylsulfonyl-2-benzylsulfonylmethyl-propionamide and *N*-(3-benzenesulfonyl-1-phenethyl-allyl)-3-benzylsulfonyl-2-benzylsulfonylmethyl-propionamide;

and the *N*-oxide derivatives, prodrug derivatives, protected derivatives, individual isomers and mixtures of isomers thereof; and the pharmaceutically acceptable salts and solvates of such compounds and the N-oxide derivatives, prodrug derivatives, protected derivatives, individual isomers and mixtures of isomers thereof.

16. The compound of claim 7 of Formula I(d):



I(d)

and the *N*-oxide derivatives, prodrug derivatives, protected derivatives, individual isomers and mixtures of isomers thereof; and the pharmaceutically acceptable salts and solvates of such compounds and the N-oxide derivatives, prodrug derivatives, protected derivatives, individual isomers and mixtures of isomers thereof.

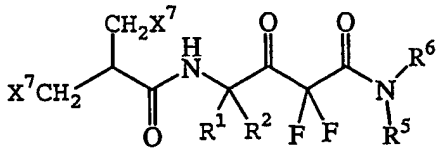
17. The compound of claim 16 in which R^5 is phenyl and R^6 is hydrogen;

and the *N*-oxide derivatives, prodrug derivatives, protected derivatives, individual isomers and mixtures of isomers thereof; and the pharmaceutically acceptable salts and solvates of such compounds and the N-oxide derivatives, prodrug derivatives, protected derivatives, individual isomers and mixtures of isomers thereof.

18. The compound of claim 17 namely *N*-(3-benzenesulfonylamino-2-oxo-propyl)-4-morpholin-4-yl-4-oxo-2-benzylsulfonylmethyl-butyramide;

and the *N*-oxide derivatives, prodrug derivatives, protected derivatives, individual isomers and mixtures of isomers thereof; and the pharmaceutically acceptable salts and solvates of such compounds and the N-oxide derivatives, prodrug derivatives, protected derivatives, individual isomers and mixtures of isomers thereof.

19. The compound of claim 7 of Formula I(e):



I(e)

and the *N*-oxide derivatives, prodrug derivatives, protected derivatives, individual isomers and mixtures of isomers thereof; and the pharmaceutically acceptable salts and solvates of such compounds and the N-oxide derivatives, prodrug derivatives, protected derivatives, individual isomers and mixtures of isomers thereof.

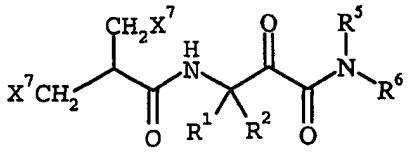
20. The compound of claim 19 in which R^5 and R^6 is methyl;

and the *N*-oxide derivatives, prodrug derivatives, protected derivatives, individual isomers and mixtures of isomers thereof; and the pharmaceutically acceptable salts and solvates of such compounds and the N-oxide derivatives, prodrug derivatives, protected derivatives, individual isomers and mixtures of isomers thereof.

21. The compound of claim 20 in which one X^7 is morpholine-4-carbonyl and the other is benzylsulfonyl, R^1 is hydrogen and R^2 is ethyl, namely (S)-2,2-difluoro-4-(4-morpholin-4-yl-4-oxo-2-benzylsulfonylmethyl-butanoylamino)-3-oxo-hexanoic acid dimethylamide;

and the *N*-oxide derivatives, prodrug derivatives, protected derivatives, individual isomers and mixtures of isomers thereof; and the pharmaceutically acceptable salts and solvates of such compounds and the N-oxide derivatives, prodrug derivatives, protected derivatives, individual isomers and mixtures of isomers thereof.

22. The compound of claim 7 of Formula I(f):



I(f)

and the *N*-oxide derivatives, prodrug derivatives, protected derivatives, individual isomers and mixtures of isomers thereof; and the pharmaceutically acceptable salts and solvates of such compounds and the N-oxide derivatives, prodrug derivatives, protected derivatives, individual isomers and mixtures of isomers thereof.

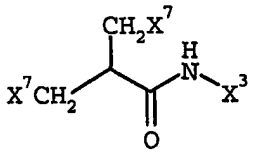
23. The compound of claim 22 in which R^5 is methyl, benzyl, phenethyl, cyclohexyl, methoxyethyl, dimethylaminoethyl, tetrahydro-pyran-4-yl, 1-methylsulfonyl-piperidin-4-yl, 4-methyl-piperazin-1-yl, morpholin-4-ylethyl, pyridin-2-yl, pyridin-2-ylmethyl or oxazol-2-ylmethyl; R^6 is hydrogen or methyl; or R^5 and R^6 together with the nitrogen atom to which both R^5 and R^6 are attached form morpholine-4-yl, pyrrolidin-1-yl, 4-dimethylamino-piperazin-1-yl, 4-hydroxy-piperazin-1-yl, 4-pyridin-2-yl-piperazin-1-yl, 4-benzoyl-piperazin-1-yl or 3-oxo-piperazin-1-yl;

and the *N*-oxide derivatives, prodrug derivatives, protected derivatives, individual isomers and mixtures of isomers thereof; and the pharmaceutically acceptable salts and solvates of such compounds and the N-oxide derivatives, prodrug derivatives, protected derivatives, individual isomers and mixtures of isomers thereof.

24. The compound of claim 23 selected from the group consisting of *N*-[(S)-1-(1-Benzylcarbamoyl-methanoyl)-propyl]-3-benzylsulfonyl-2-benzylsulfonylmethyl-propionamide and *N*-[(S)-1-(1-Benzylcarbamoyl-methanoyl)-propyl]-4-morpholin-4-yl-4-oxo-2-benzylsulfonylmethyl-butyramide;

and the *N*-oxide derivatives, prodrug derivatives, protected derivatives, individual isomers and mixtures of isomers thereof; and the pharmaceutically acceptable salts and solvates of such compounds and the N-oxide derivatives, prodrug derivatives, protected derivatives, individual isomers and mixtures of isomers thereof.

25. The compound of claim 7 of Formula I(g):



I(g)

and the *N*-oxide derivatives, prodrug derivatives, protected derivatives, individual isomers and mixtures of isomers thereof; and the pharmaceutically acceptable salts and solvates of such compounds and the N-oxide derivatives, prodrug derivatives, protected derivatives, individual isomers and mixtures of isomers thereof.

26. The compound of claim 25 in which X^3 is 1-benzoyl-4-oxo-pyrrolidin-3-yl, 4-oxo-pyrrolidin-3-yl-1-carboxylic acid tert-butyl ester, 2-methyl-4-oxo-tetrahydro-furan-3-yl, 2-ethyl-4-oxo-tetrahydro-furan-3-yl, 4-oxo-tetrahydro-furan-3-yl, 2-acetoxy-4-oxo-azetidin-3-yl, 1-isopropyl-3-oxo-azepan-4-yl, 3-oxo-azepan-4-yl-1-carboxylic acid benzyl ester, 3-oxo-azepan-4-yl-1-carboxylic acid tert-butyl ester, 1-benzoyl-3-oxo-azepan-4-yl, 1-isobutyryl-3-oxo-azepan-4-yl, 3-oxo-1-(propane-2-sulfonyl)-azepan-4-yl, 1-benzenesulfonyl-3-oxo-azepan-4-yl, 1-benzenesulfonyl-3-oxo-piperidin-4-yl, 1-benzenesulfonyl-4-oxo-pyrrolidin-3-yl, 1-benzoyl-3-oxo-piperidin-4-yl or 3-oxo-tetrahydro-pyran-4-yl;

and the *N*-oxide derivatives, prodrug derivatives, protected derivatives, individual isomers and mixtures of isomers thereof; and the pharmaceutically acceptable salts and solvates of such compounds and the N-oxide derivatives, prodrug derivatives, protected derivatives, individual isomers and mixtures of isomers thereof.

27. The compound of claim 23 selected from the group consisting of 3-Hydroxy-4-(4-morpholin-4-yl-4-oxo-2-benzylsulfonylmethyl-butyrylamino)-azepane-1-carboxylic acid tert-butyl ester; 4-(2-Cyclopropylmethylsulfonylmethyl-4-morpholin-4-yl-4-oxo-butyrylamino)-3-hydroxy-azepane-1-carboxylic acid tert-butyl ester; 3-Hydroxy-4-[2-(2-methyl-propane-1-sulfonylmethyl)-4-morpholin-4-yl-4-oxo-butyrylamino]-azepane-1-carboxylic acid tert-butyl ester; 4-(4-Morpholin-4-yl-4-oxo-2-benzylsulfonylmethyl-

butyrylamino)-3-oxo-azepane-1-carboxylic acid tert-butyl ester; 4-(2-Cyclopropylmethylsulfonylmethyl-4-morpholin-4-yl-4-oxo-butyrylamino)-3-oxo-azepane-1-carboxylic acid tert-butyl ester; 4-[2-(2-Methyl-propane-1-sulfonylmethyl)-4-morpholin-4-yl-4-oxo-butyrylamino]-3-oxo-azepane-1-carboxylic acid tert-butyl ester; *N*-(1-Benzenesulfonyl-3-oxo-azepan-4-yl)-4-morpholin-4-yl-4-oxo-2-benzylsulfonylmethyl-butyramide; *N*-(1-Benzenesulfonyl-3-oxo-azepan-4-yl)-2-(2-methyl-propane-1-sulfonylmethyl)-4-morpholin-4-yl-4-oxo-butyramide; 3-(4-Morpholin-4-yl-4-oxo-2-benzylsulfonylmethyl-butyrylamino)-4-oxo-pyrrolidine-1-carboxylic acid tert-butyl ester; 4-(4-Morpholin-4-yl-4-oxo-2-benzylsulfonylmethyl-butyrylamino)-3-oxo-azepane-1-carboxylic acid benzyl ester; and acetic acid (2S,3S)-3-(4-morpholin-4-yl-4-oxo-2-benzylsulfonylmethyl-butanoylamino)-4-oxo-azetidin-2-yl ester;

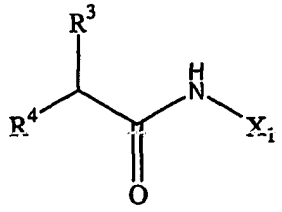
and the *N*-oxide derivatives, prodrug derivatives, protected derivatives, individual isomers and mixtures of isomers thereof; and the pharmaceutically acceptable salts and solvates of such compounds and the N-oxide derivatives, prodrug derivatives, protected derivatives, individual isomers and mixtures of isomers thereof.

28. A pharmaceutical composition comprising a therapeutically effective amount of a compound of Claim 1 in combination with a pharmaceutically acceptable excipient.

29. A method for treating a disease in an animal in which inhibition of Cathepsin S can prevent, inhibit or ameliorate the pathology and/or symptomology of the disease, which method comprises administering to the animal a therapeutically effective amount of compound of Claim 1 or a *N*-oxide derivative or individual isomer or mixture of isomers thereof; or a pharmaceutically acceptable salt or solvate of such compounds and the *N*-oxide derivatives, prodrug derivatives, protected derivatives, individual isomers and mixtures of isomers thereof.

30. The use of a compound of Claim 1 in the manufacture of a medicament for treating a disease in an animal in which Cathepsin S activity contributes to the pathology and/or symptomology of the disease.

31. A process for preparing a compound of Formula I:



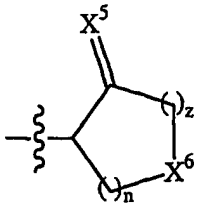
I

in which:

X^1 is $-C(R^1)(R^2)X^2$ or $-X^3$;

X^2 is cyano, -CHO, $-C(R^7)(R^8)R^5$, $-C(R^7)(R^8)CF_3$, $-C(R^7)(R^8)CF_2CF_2R^9$ $-CH{=}CHS(O)_2R^5$, $-C(R^7)(R^8)CF_2C(O)NR^5R^6$, $-C(R^7)(R^8)C(R^7)(R^8)NR^5R^6$, $-C(R^7)(R^8)C(R^7)(R^8)OR^5$, $-C(R^7)(R^8)CH_2OR^5$, $-C(R^7)(R^8)CH_2N(R^6)SO_2R^5$, $-C(R^7)(R^8)C(R^7)(R^8)N(R^6)(CH_2)_2OR^6$, $-C(R^7)(R^8)C(R^7)(R^8)N(R^6)(CH_2)_2NR^6$ or $-C(R^7)(R^8)C(R^7)(R^8)R^5$; wherein R^5 is (C_{1-4})alkyl, (C_{6-10})aryl(C_{0-6})alkyl, hetero(C_{4-10})aryl(C_{0-6})alkyl, (C_{4-10})cycloalkyl(C_{0-6})alkyl or hetero(C_{4-10})cycloalkyl(C_{0-6})alkyl; R^6 is hydrogen or (C_{1-6})alkyl; R^7 is hydrogen or (C_{1-4})alkyl and R^8 is hydroxy or R^7 and R^8 together form oxo; R^9 is hydrogen, halo, (C_{1-4})alkyl, (C_{5-10})aryl(C_{0-6})alkyl or hetero(C_{5-10})aryl(C_{0-6})alkyl;

X^3 represents a group of Formula (a):



(a)

in which n is 1 or 2, z is 0 or 1, X^5 is selected from NR^{10}, S or O, wherein R^{10} is hydrogen or (C_{1-6})alkyl, and X^6 is O, S or NR^{11}, wherein R^{11} is selected from hydrogen, (C_{1-6})alkyl, $-X^4C(O)OR^{12}$, $-X^4C(O)R^{13}$, $-X^4C(O)NR^{12}R^{12}$, $-X^4S(O)_2NR^{12}R^{12}$, $-X^4S(O)_2R^{14}$, $-R^{15}$, $-X^4S(O)_2R^{15}$, $-X^4C(O)R^{15}$, $-X^4C(O)OR^{15}$, $-X^4C(O)NR^{12}R^{15}$ and $-X^4S(O)_2NR^{12}R^{15}$, in which X^4 is a bond or (C_{1-6})alkylene; R^{12} at each occurrence independently is hydrogen or (C_{1-6})alkyl; R^{13} is hydrogen, (C_{1-6})alkyl or halo-substituted(C_{1-6})alkyl, R^{14} is (C_{1-6})alkyl or halo-substituted(C_{1-6})alkyl and R^{15} is (C_{3-10})cycloalkyl(C_{0-6})alkyl, hetero(C_{3-10})cycloalkyl(C_{0-3})alkyl, (C_{6-10})aryl(C_{0-6})alkyl, hetero(C_{5-10})aryl(C_{0-6})alkyl, (C_{9-12})bicycloaryl(C_{0-6})alkyl or hetero(C_{8-12})bicycloaryl(C_{0-6})alkyl;

wherein within X^1 any cycloalkyl, heterocycloalkyl, aryl or heteroaryl may be substituted with 1 radical R^{20} selected from $-R^{15}$, $-X^4OR^{15}$, $-X^4SR^{15}$, $-X^4S(O)R^{15}$, $-X^4S(O)_2R^{15}$, $-X^4C(O)R^{15}$, $-X^4C(O)OR^{15}$, $-X^4OC(O)R^{15}$, $-X^4NR^{15}R^{12}$, $-X^4NR^{12}C(O)R^{15}$, $-X^4NR^{12}C(O)OR^{15}$, $-X^4C(O)NR^{15}R^{12}$, $-X^4S(O)_2NR^{15}R^{12}$, $-X^4NR^{12}S(O)_2R^{15}$, $-X^4NR^{12}C(O)NR^{15}R^{12}$ and $-X^4NR^{12}C(NR^{12})NR^{15}R^{12}$; and wherein X^1 and R^{20} may be substituted further with 1 to 5 radicals independently selected from (C_{1-6})alkyl, cyano, halo, halo-substituted(C_{1-4})alkyl, nitro, $-X^4NR^{12}R^{12}$, $-X^4NR^{12}C(O)R^{12}$, $-X^4NR^{12}C(O)OR^{12}$, $-X^4NR^{12}C(O)NR^{12}R^{12}$, $-X^4NR^{12}C(NR^{12})NR^{12}R^{12}$, $-X^4OR^{13}$, $-X^4SR^{13}$, $-X^4C(O)OR^{12}$, $-X^4C(O)R^{13}$, $-X^4OC(O)R^{13}$, $-X^4C(O)NR^{12}R^{12}$, $-X^4S(O)_2NR^{12}R^{12}$, $-X^4NR^{12}S(O)_2R^{13}$, $-X^4P(O)(OR^{12})OR^{12}$, $-X^4OP(O)(OR^{12})OR^{12}$, $-X^4S(O)R^{14}$ and $-X^4S(O)_2R^{14}$ wherein X^4, R^{12}, R^{13}, R^{14} and R^{15} are as defined above;

R^1 and R^2 are both fluoro; or

R^1 is hydrogen or (C_{1-6})alkyl and R^2 is selected from the group consisting of hydrogen, (C_{1-6})alkyl, cyano, $-X^4NR^{12}R^{12}$, $-X^4NR^{12}C(O)R^{12}$, $-X^4NR^{12}C(O)OR^{12}$, $-X^4NR^{12}C(O)NR^{12}R^{12}$, $-X^4NR^{12}C(NR^{12})NR^{12}R^{12}$, $-X^4OR^{13}$, $-X^4SR^{13}$, $-X^4C(O)OR^{12}$, $-X^4C(O)R^{13}$, $-X^4OC(O)R^{13}$, $-X^4C(O)NR^{12}R^{12}$, $-X^4S(O)_2NR^{12}R^{12}$, $-X^4NR^{12}S(O)_2R^{13}$, $-X^4P(O)(OR^{12})OR^{12}$, $-X^4OP(O)(OR^{12})OR^{12}$, $-X^4S(O)R^{14}$, $-X^4S(O)_2R^{14}$, $-R^{15}$, $-X^4OR^{15}$, $-X^4SR^{15}$, $-X^4S(O)R^{15}$, $-X^4S(O)_2R^{15}$, $-X^4C(O)R^{15}$, $-X^4C(O)OR^{15}$, $-X^4OC(O)R^{15}$, $-X^4NR^{15}R^{12}$, $-X^4NR^{12}C(O)R^{15}$, $-X^4NR^{12}C(O)OR^{15}$, $-X^4C(O)NR^{15}R^{12}$, $-X^4S(O)_2NR^{15}R^{12}$, $-X^4NR^{12}S(O)_2R^{15}$, $-X^4NR^{12}C(O)NR^{15}R^{12}$ and $-X^4NR^{12}C(NR^{12})NR^{15}R^{12}$, wherein X^4, R^{12}, R^{13}, R^{14} and R^{15} are as defined above; or R^1 and R^2 taken together with the carbon atom to which both R^1 and R^2 are attached form (C_{3-8})cycloalkylene or hetero(C_{3-8})cycloalkylene;

wherein R^2, said cycloalkylene and said heterocycloalkylene may be substituted further with 1 to 3 radicals independently selected from (C_{1-6})alkyl, cyano, halo, halo-substituted(C_{1-4})alkyl, nitro, $-X^4NR^{12}R^{12}$, $-X^4NR^{12}C(O)R^{12}$, $-X^4NR^{12}C(O)OR^{12}$, $-X^4NR^{12}C(O)NR^{12}R^{12}$, $-X^4NR^{12}C(NR^{12})NR^{12}R^{12}$, $-X^4OR^{13}$, $-X^4SR^{13}$, $-X^4C(O)OR^{12}$, $-X^4C(O)R^{13}$, $-X^4OC(O)R^{13}$, $-X^4C(O)NR^{12}R^{12}$, $-X^4S(O)_2NR^{12}R^{12}$, $-X^4NR^{12}S(O)_2R^{13}$, $-X^4P(O)(OR^{12})OR^{12}$, $-X^4OP(O)(OR^{12})OR^{12}$, $-X^4S(O)R^{14}$ and $-X^4S(O)_2R^{14}$, wherein X^4, R^{12}, R^{13} and R^{14} are as defined above;

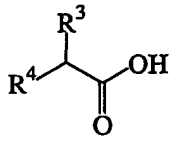
R^3 and R^4 are independently $-C(R^{16})(R^{17})X^7$, wherein R^{16} and R^{17} are hydrogen, (C_{1-6})alkyl or fluoro, or R^{16} is hydrogen and R^{17} is hydroxy and X^7 is selected from $-X^4NR^{12}R^{12}$, $-X^4NR^{12}C(O)R^{12}$, $-X^4NR^{12}C(O)OR^{12}$, $-X^4NR^{12}C(O)NR^{12}R^{12}$, $-X^4NR^{12}C(NR^{12})NR^{12}R^{12}$, $-X^4OR^{13}$, $-X^4SR^{13}$, $-X^4C(O)OR^{12}$, $-X^4C(O)R^{13}$, $-X^4OC(O)R^{13}$, $-X^4C(O)NR^{12}R^{12}$, $-X^4S(O)_2NR^{12}R^{12}$, $-X^4NR^{12}S(O)_2R^{13}$, $-X^4P(O)(OR^{12})OR^{12}$, $-X^4OP(O)(OR^{12})OR^{12}$, $-X^4S(O)R^{14}$, $-X^4S(O)_2R^{14}$, $-R^{15}$, $-X^4OR^{15}$, $-X^4SR^{15}$, $-X^4S(O)R^{15}$, $-X^4S(O)_2R^{15}$, $-X^4C(O)R^{15}$, $-X^4C(O)OR^{15}$, $-X^4OC(O)R^{15}$, $-X^4NR^{15}R^{12}$, $-X^4NR^{12}C(O)R^{15}$, $-X^4NR^{12}C(O)OR^{15}$, $-X^4C(O)NR^{15}R^{12}$, $-X^4S(O)_2NR^{15}R^{12}$, $-X^4NR^{12}S(O)_2R^{15}$, $-X^4NR^{12}C(O)NR^{15}R^{12}$ and $-X^4NR^{12}C(NR^{12})NR^{15}R^{12}$, wherein X^4, R^{12}, R^{13}, R^{14} and R^{15} are as defined above;

wherein within one of R^3 or R^4 any cycloalkyl, heterocycloalkyl, aryl or heteroaryl may be substituted with 1 radical R^{21} selected from $-R^{15}$, $-X^4OR^{15}$, $-X^4SR^{15}$, $-X^4S(O)R^{15}$, $-X^4S(O)_2R^{15}$, $-X^4C(O)R^{15}$, $-X^4C(O)OR^{15}$, $-X^4OC(O)R^{15}$, $-X^4NR^{15}R^{12}$, $-X^4NR^{12}C(O)R^{15}$, $-X^4NR^{12}C(O)OR^{15}$, $-X^4C(O)NR^{12}R^{15}$, $-X^4S(O)_2NR^{15}R^{12}$, $-X^4NR^{12}S(O)_2R^{15}$, $-X^4NR^{12}C(O)NR^{15}R^{12}$ and $-X^4NR^{12}C(NR^{12})NR^{15}R^{12}$, wherein X^4, R^{12} and R^{15} are as defined above; and wherein each of R^3, R^4 and R^{21} may be substituted further with 1 to 5 radicals independently selected from (C_{1-6})alkyl, cyano, halo, halo-substituted(C_{1-4})alkyl, nitro, $-X^4NR^{12}R^{12}$, $-X^4NR^{12}C(O)R^{12}$, $-X^4NR^{12}C(O)OR^{12}$, $-X^4NR^{12}C(O)NR^{12}R^{12}$, $-X^4NR^{12}C(NR^{12})NR^{12}R^{12}$, $-X^4OR^{13}$, $-X^4SR^{13}$, $-X^4C(O)OR^{12}$, $-X^4C(O)R^{13}$, $-X^4OC(O)R^{13}$, $-X^4C(O)NR^{12}R^{12}$, $-X^4S(O)_2NR^{12}R^{12}$, $-X^4NR^{12}S(O)_2R^{13}$, $-X^4P(O)(OR^{12})OR^{12}$, $-X^4OP(O)(OR^{12})OR^{12}$, $-X^4S(O)R^{14}$ and $-X^4S(O)_2R^{14}$, wherein X^4, R^{12}, R^{13} and R^{14} are as defined above; provided that only one bicyclic ring structure is present within each of R^3 or R^4; and provided that when X^2 is cyano and X^7 within one of R^3 or R^4 is $-X^4C(O)R^{13}$ or $-X^4C(O)R^{15}$, wherein X^4 is a bond, then X^7 within the other of R^3 or R^4 is limited to

$-X^4SR^{15}$, $-X^4S(O)R^{15}$ and $-X^4S(O)_2R^{15}$, wherein R^{15} is (C_{6-10})aryl(C_{1-6})alkyl substituted with 1 to 5 radicals or hetero(C_{5-10})aryl(C_{0-6})alkyl optionally substituted with 1 to 5 radicals, wherein said radicals are independently selected from (C_{1-6})alkyl, cyano, halo, halo-substituted(C_{1-4})alkyl, nitro, $-X^4NR^{12}R^{12}$, $-X^4NR^{12}C(O)R^{12}$, $-X^4NR^{12}C(O)OR^{12}$, $-X^4NR^{12}C(O)NR^{12}R^{12}$, $-X^4NR^{12}C(NR^{12})NR^{12}R^{12}$, $-X^4OR^{13}$, $-X^4SR^{13}$, $-X^4C(O)OR^{12}$, $-X^4C(O)R^{13}$, $-X^4OC(O)R^{13}$, $-X^4C(O)NR^{12}R^{12}$, $-X^4S(O)_2NR^{12}R^{12}$, $-X^4NR^{12}S(O)_2R^{13}$, $-X^4P(O)(OR^{12})OR^{12}$, $-X^4OP(O)(OR^{12})OR^{12}$, $-X^4S(O)R^{14}$ and $-X^4S(O)_2R^{14}$, wherein X^4, R^{12}, R^{13} and R^{14} are as defined above, provided that the radical is not selected from only halo when R^{15} is (C_{6-10})aryl(C_{1-6})alkyl; and provided that when X^2 is cyano then X^7 within R^3 and R^4 is not $-X^4C(O)NR^{12}R^{12}$, $-X^4C(O)NR^{15}R^{12}$ or $-X^4C(O)NR^{18}R^{19}$, wherein X^4 is a bond and R^{18} and R^{19} together with the nitrogen atom to which they are attached form hetero(C_{3-10})cycloalkyl or hetero(C_{5-10})aryl;

and the corresponding N-oxides, and their prodrugs, and their protected derivatives, individual isomers and mixtures of isomers thereof; and the pharmaceutically acceptable salts and solvates of such compounds of formula I and their N-oxides and their prodrugs, and their protected derivatives, individual isomers and mixtures of isomers thereof; which process comprises:

(A) reacting a compound of Formula 2:



2

with a compound of the formula $NH_2CR^1R^2X^2$, in which X^2, R^1, R^2, R^3 and R^4 are as defined in the Summary of the Invention for Formula I; or

(B) reacting a compound of Formula 2 with a compound of the formula NH_2X^3, in which X^3, R^3 and R^4 are as defined in the Summary of the Invention for Formula I; or

(C) optionally converting a compound of Formula I into a pharmaceutically acceptable salt;

(D) optionally converting a salt form of a compound of Formula I to non-salt form;

(E) optionally converting an unoxidized form of a compound of Formula I into a pharmaceutically acceptable *N*-oxide;

(F) optionally converting an *N*-oxide form of a compound of Formula I its unoxidized form;

(G) optionally resolving an individual isomer of a compound of Formula I from a mixture of isomers;

(H) optionally converting a non-derivatized compound of Formula I into a pharmaceutically prodrug derivative; and

(I) optionally converting a prodrug derivative of a compound of Formula I to its non-derivatized form.